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High-Throughput Synthesis and Analysis for Searching New Permanent Magnet Materials

Gerhard Schneider
Materials Research Institute, Aalen University

Dagmar Goll
Materials Research Institute, Aalen University

Ralf Loffller
Materials Research Institute, Aalen University

Roman Karimi

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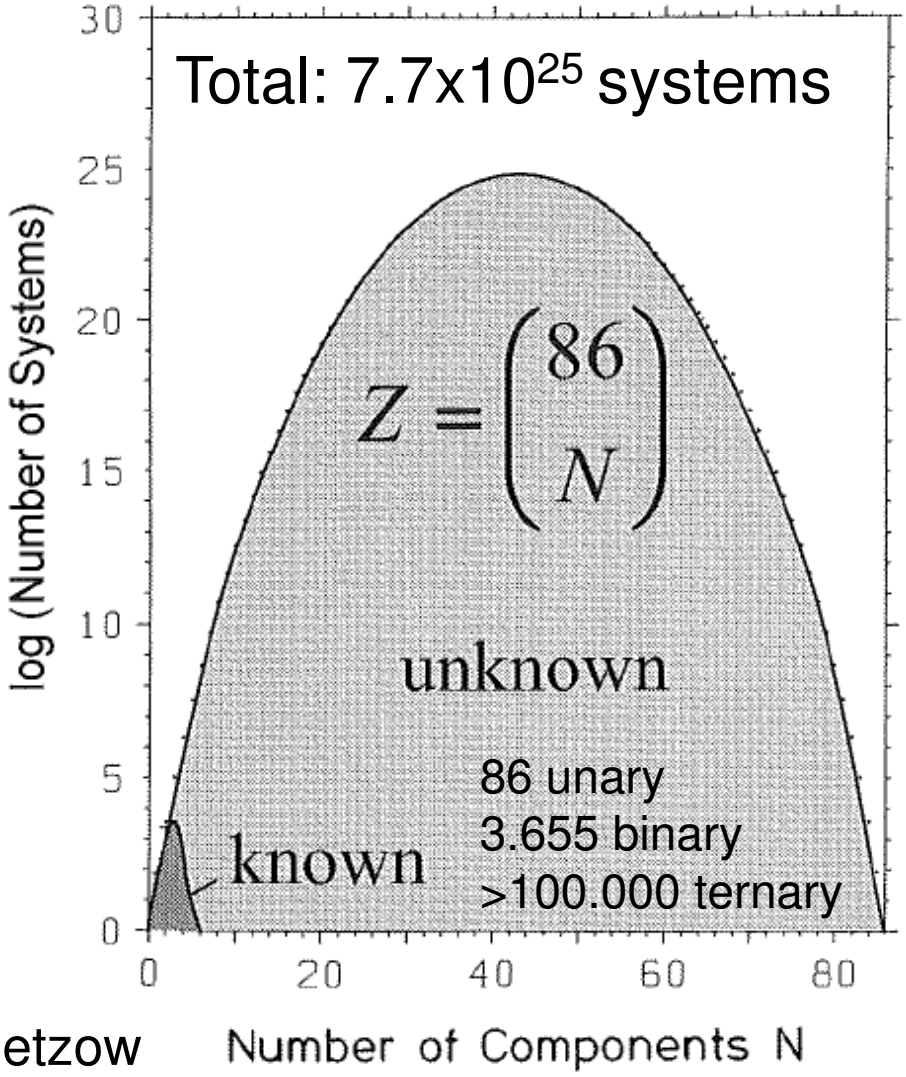
Aalen University, Materials Research Institute, Germany

- Motivation for searching new magnetic materials
- Selection of systems, prioritization
- High-throughput synthesis
- High-throughput analysis

Aalen University

Potential to discover new materials



Petzow

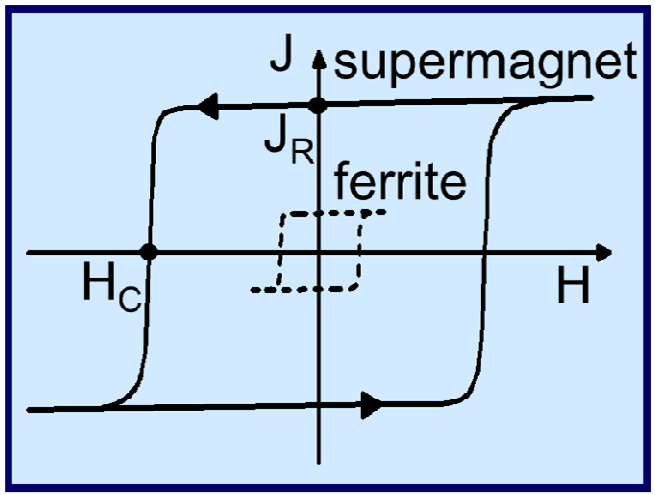
Still great potential to find new materials with specific properties.

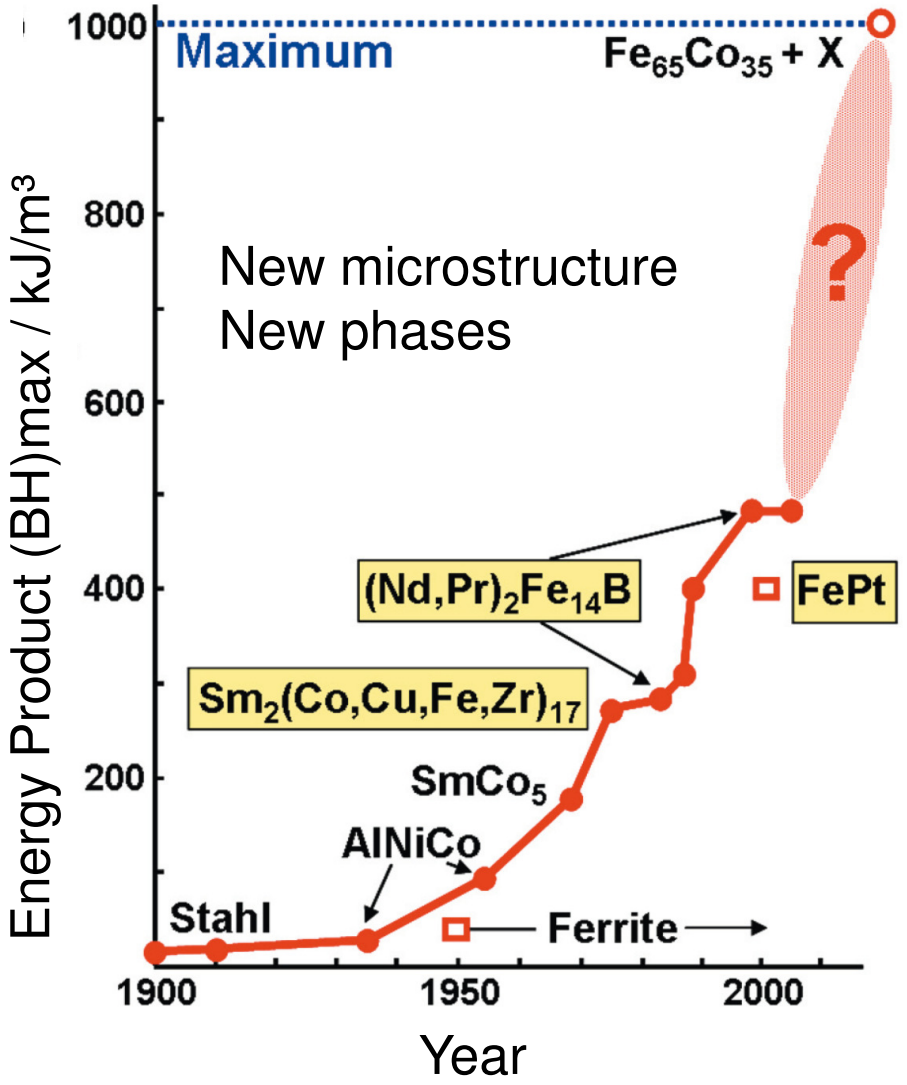
Need to develop High-Throughput methods

Motivation for the search of new magnetic phases

Key applications in energy conversion

- Generators
- Motors

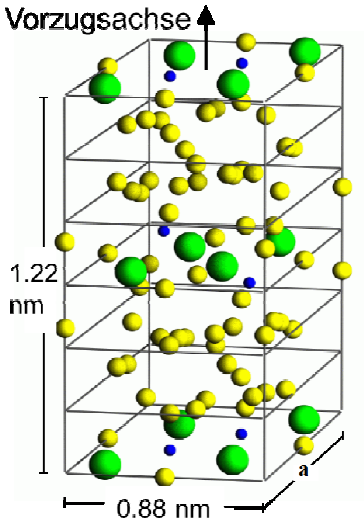




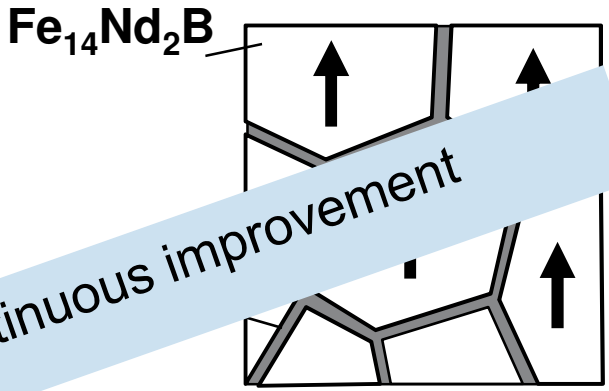
Preconditions for permanent magnets

- Existence/ stability of a phase with excellent intrinsic properties – $Fe_{14}Nd_2B$
  - Magnetocrystalline anisotropy H_A = 68 MA/m
  - Saturation polarization J_s = 1.63 T
  - Curie temperature T_C = 310 °C
  - …

disruptive



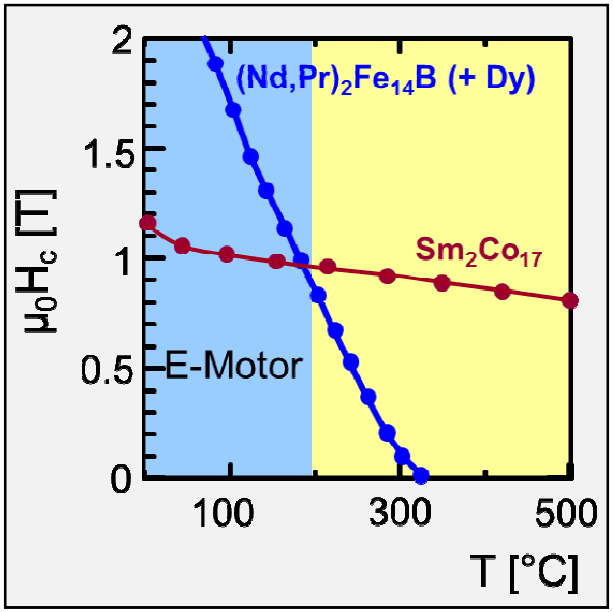
- Microstructure design – extrinsic properties
  - Avoid soft magnetic phases
  - Isolate aligned single crystal grains magnetically
  - Avoid nonmagnetic grains



Continuous improvement

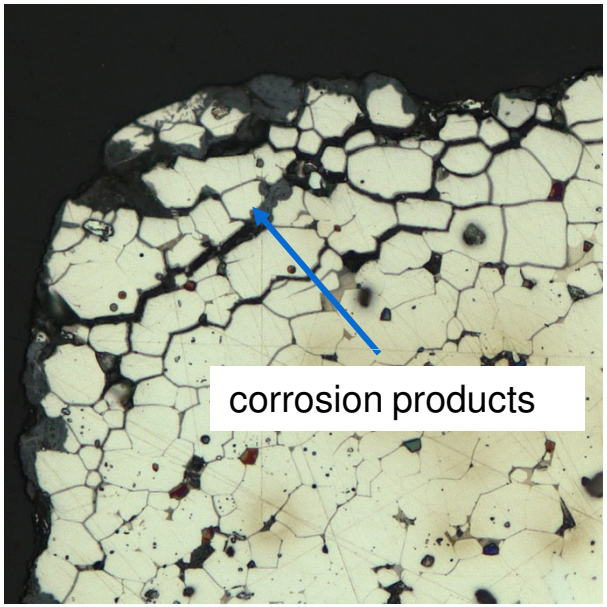
Additional requirements for permanent magnets

Temperature stability



max. operating Temperature of Fe-Nd-B: 180 °C to 200 °C

Corrosion stability



corrosion protection

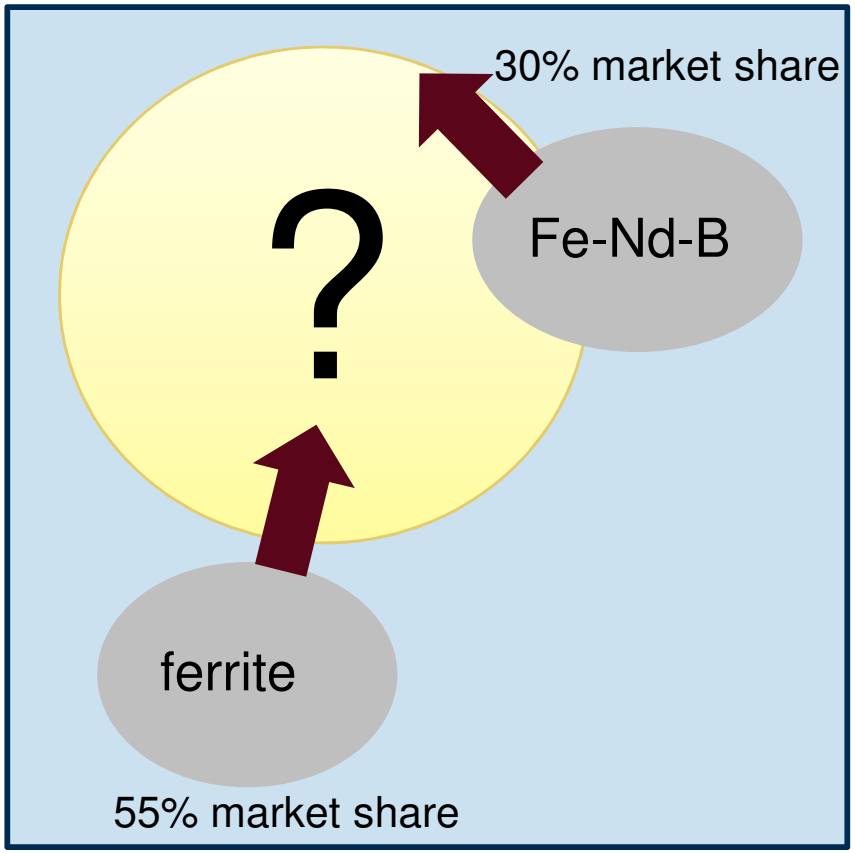
Raw material aspect

content in earth crust:
Nd: 22 ppm
Dy: 4.3 ppm

rare earth metals are expensive (97 % China)

New Permanent Magnet Materials

max. energy product $(BH)_{max}$

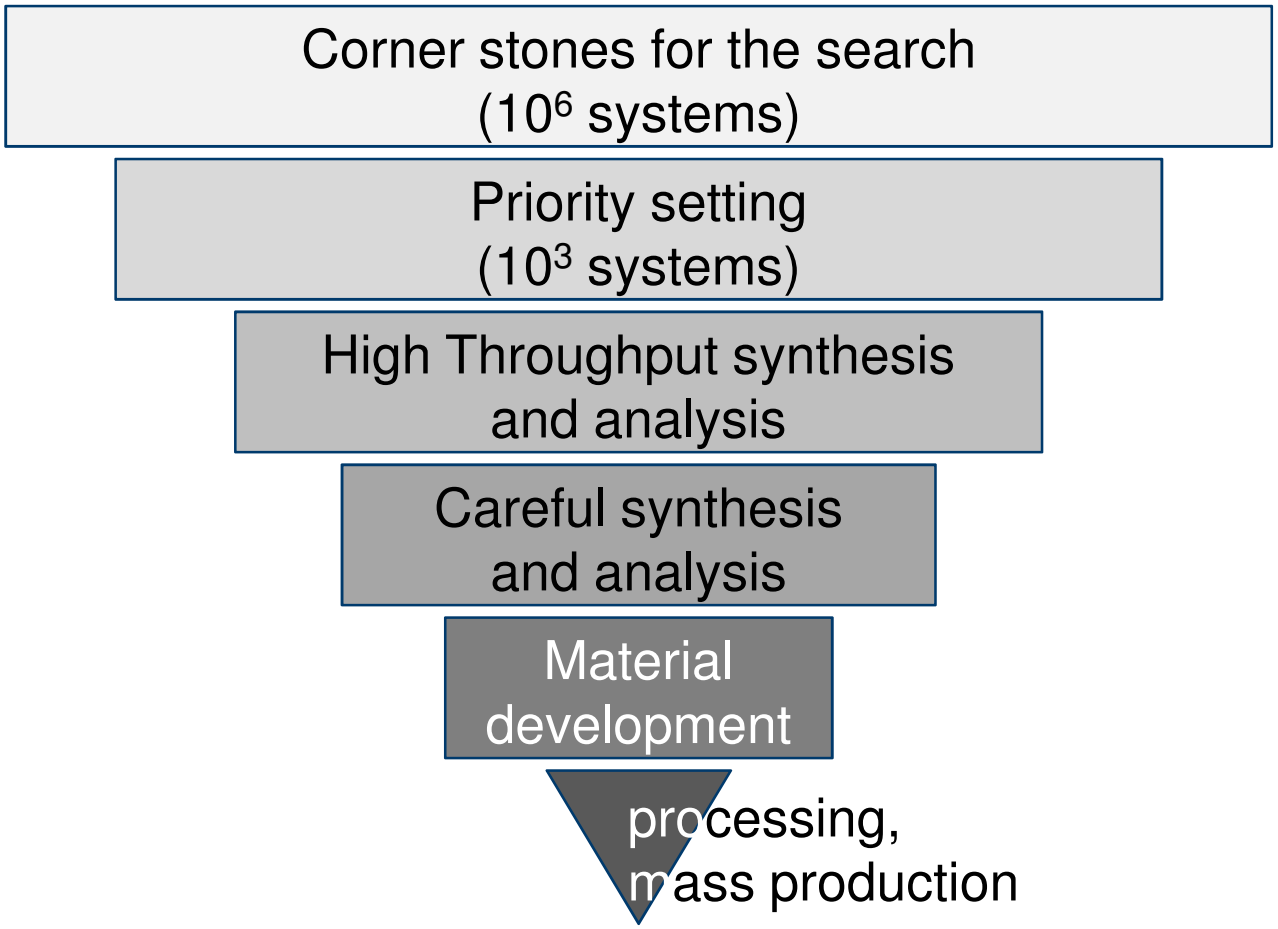


costs

Development goals:

- Magnetic performance (B_R, H_C, T_C, losses, …)
- Lower material and processing costs, availability of raw materials
- Durability (aging, corrosion, mechanical properties, …)

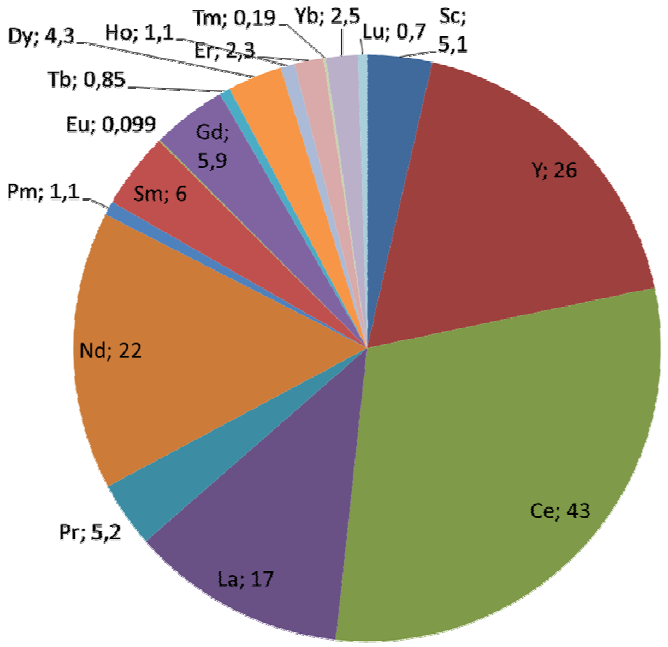
Strategy High-Throughput experimentation



First selection of elements

- Ferromagnetic transition metals (TM)
  - Basis of ferromagnetism
    (high saturation polarization, high Curie temperature)
  - Economical

RE content in earth crust [ppm]



- Rare earth metals (RE)
  - Prerequisite for highest anisotropies
  - Mischmetals are cheaper than pure RE
  - Light RE are cheaper than heavy RE
  - La or Ce are available in larger amounts

- Additives
  - for stabilization of new phases or improving properties of known phases
  - non-toxic, non-radioactive

Estimation of the number of systems

- Selection of elements
  - TM: transition metals: Fe, Co, Ni, Mn; k = 4
  - RE: rare earth metals: La, Ce, Y, Pr, Nd, Sm, Dy; j = 7
  - Add: additives X; l = 41

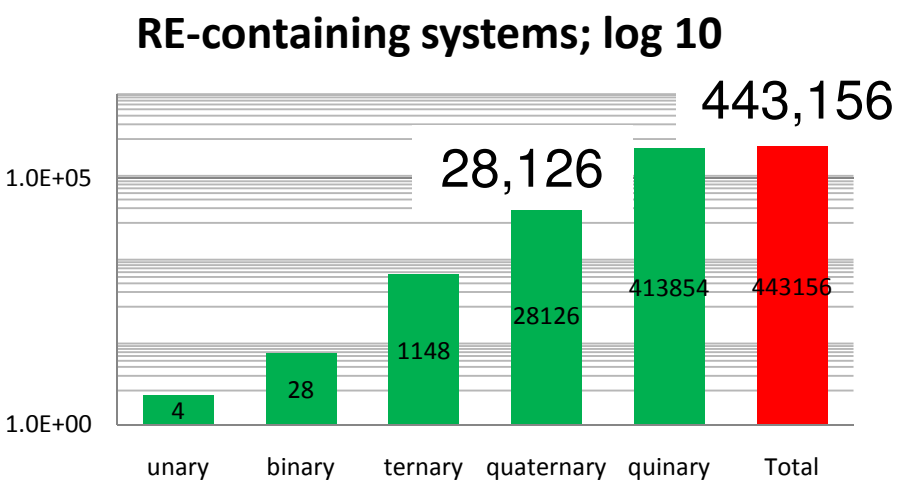
- RE systems
  - TM (unary), TM-RE (binary), TM-RE-X (ternary)
  - TM1-TM2-RE-X, TM-RE1-RE2-X, TM-RE-X1-X2 (quaternary)

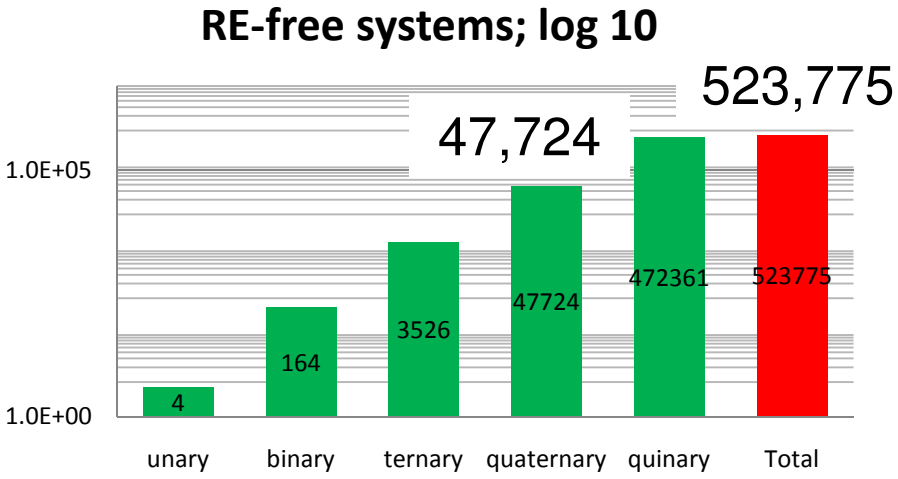
$$\binom{TM}{k}\binom{Add}{l}\binom{RE}{j} = \frac{TM!}{(TM-k)!k!}\,\frac{Add!}{(Add-l)!l!}\,\frac{RE!}{(RE-j)!j!}$$

- RE-free systems
  - TM (unary), TM-X (binary), TM1-TM2-X (ternary), TM-X1-X2 (ternary)

$$\binom{TM}{k}\binom{Add}{l} = \frac{TM!}{(TM-k)!k!}\,\frac{Add!}{(Add-l)!l!}$$

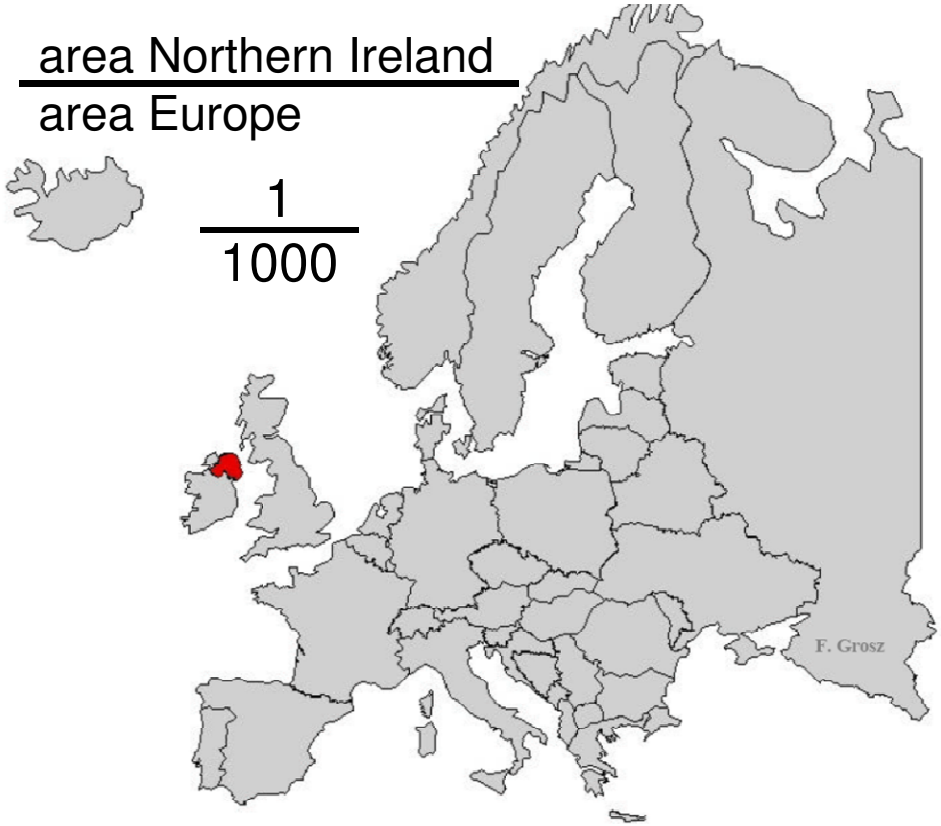
Estimation of the number of interesting systems





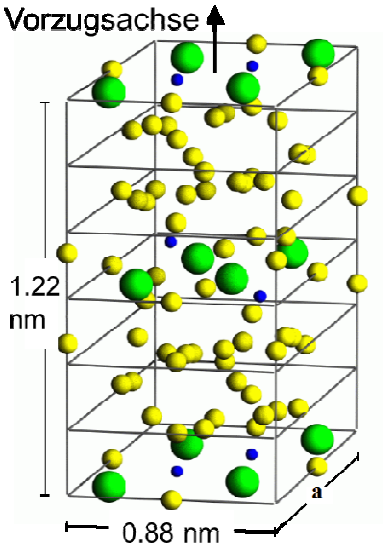
total number of systems: ~ 1.000.000
known systems: ~ 1000
ratio: ~ 1:1000

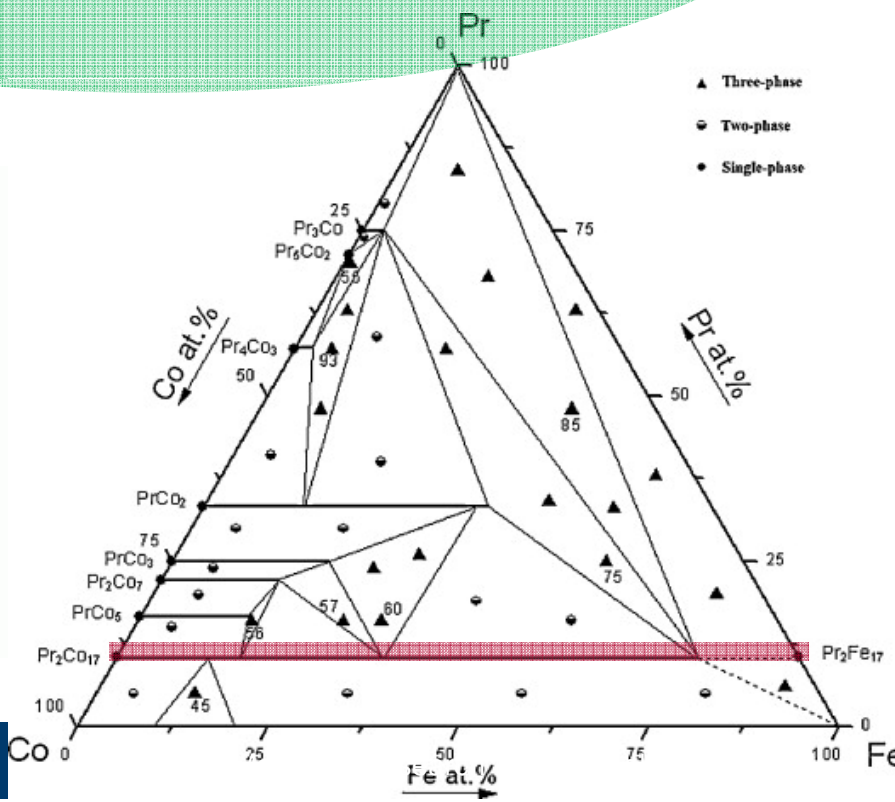
$$\frac{\text{area Northern Ireland}}{\text{area Europe}} \approx \frac{1}{1000}$$

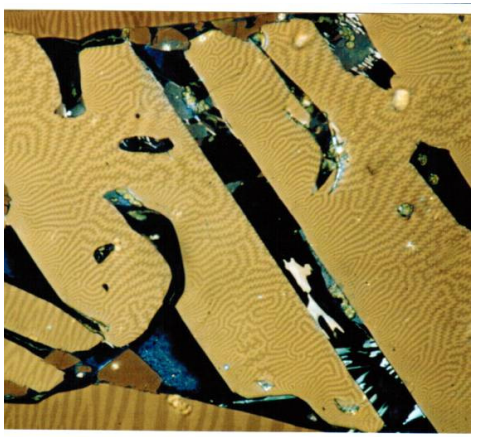


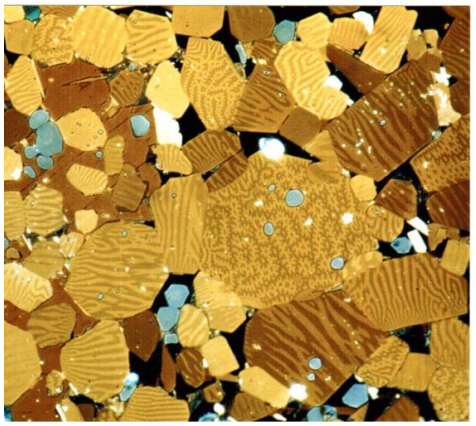
New Phases and modification of known phases

- New Phases
  - New composition
  - New crystal structure
  - Examples:
    - $Fe_{14}Nd_2B$
- Known Phases
  - Homogeneity range
  - Additives
  - Examples:
    - $(Fe,Co)_{17}Pr_2$
- Microstructure optimization

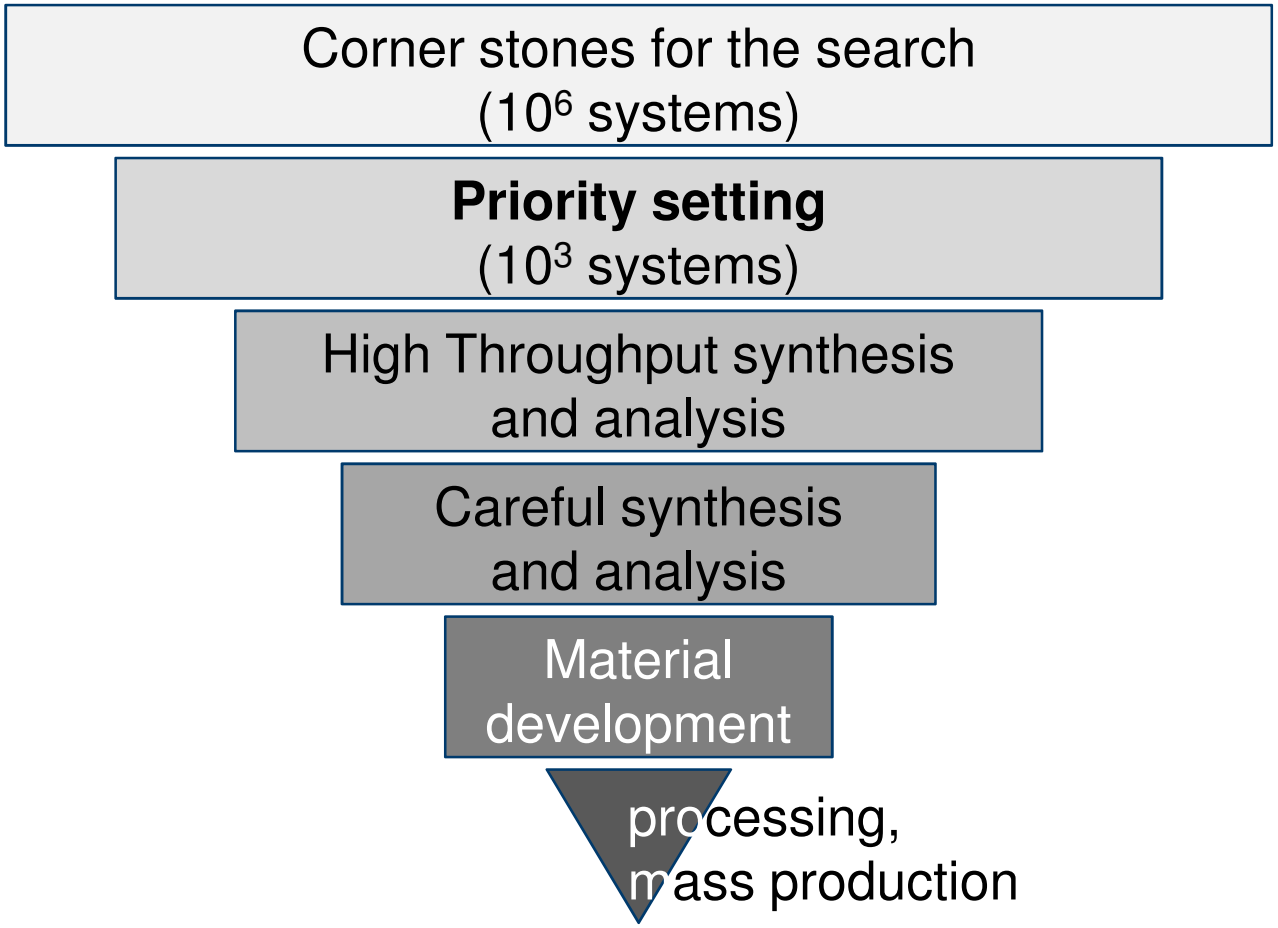




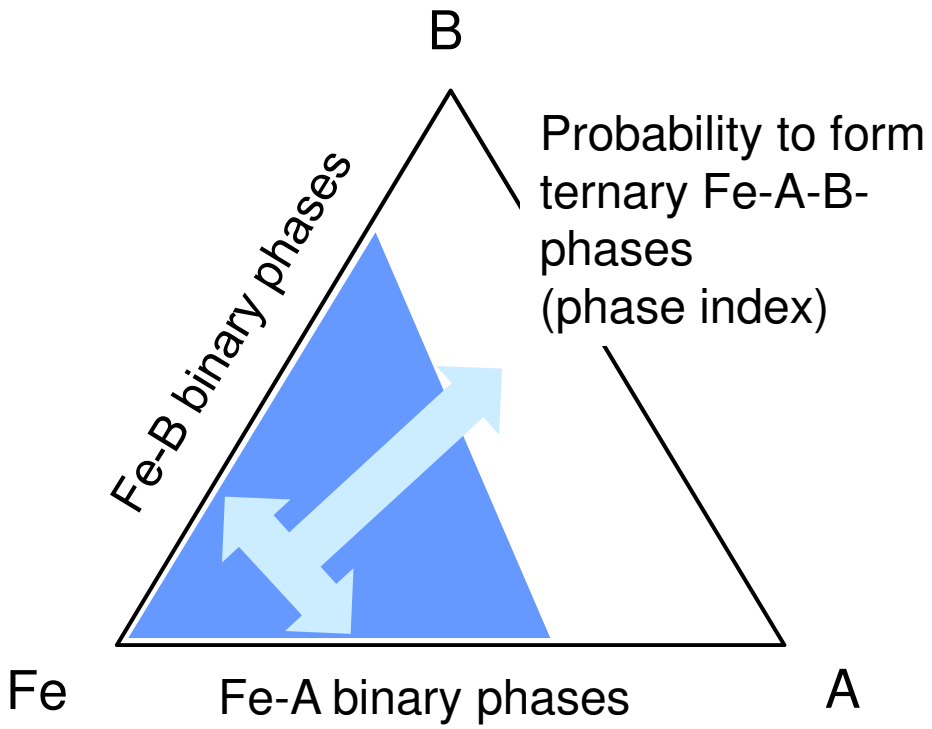




Strategy High-Throughput experimentation



Prioritization



Input data base

Fe	Element	Ag	Al	Am	As	Au	B	Ba	Be	Bi	C	Ca	Cd	Ce	Co	Cr	Cs	Cu	Dy	Er	Eu	Ga	Gd	Ge
Element	Anzahl Phasen	0	8	1	4	0	3	0	4	0	6	0	0	2	1	1	0	0	4	4	0	5	4	6
Ag	0	x	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Al	8	0	x	8	32	0	24	0	32	0	48	0	0	16	8	8	0	0	32	32	0	40	32	48
Am	1	0	8	x	4	0	3	0	4	0	6	0	0	2	1	1	0	0	4	4	0	5	4	6
As	4	0	32	4	x	0	12	0	16	0	24	0	0	8	4	4	0	0	16	16	0	20	16	24
Au	0	0	0	0	0	x	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
B	3	0	24	3	12	0	x	0	12	0	18	0	0	6	3	3	0	0	12	12	0	15	12	18
Ba	0	0	0	0	0	0	0	x	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Be	4	0	32	4	16	0	12	0	x	0	24	0	0	8	4	4	0	0	16	16	0	20	16	24
Bi	0	0	0	0	0	0	0	0	0	x	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C	6	0	48	6	24	0	18	0	24	0	x	0	0	12	6	6	0	0	24	24	0	30	24	36

List of prioritization

System	PI * KI
Fe-Y-	5
Fe-Sm-	6
Fe-Ce-	9
Fe-Y-	26
Fe-Y-	28
Fe-Y-	48
Fe-Sm-	48
Fe-Y-	50
Fe-Sm-	60
Fe-Nd-	72
Fe-Y-	72

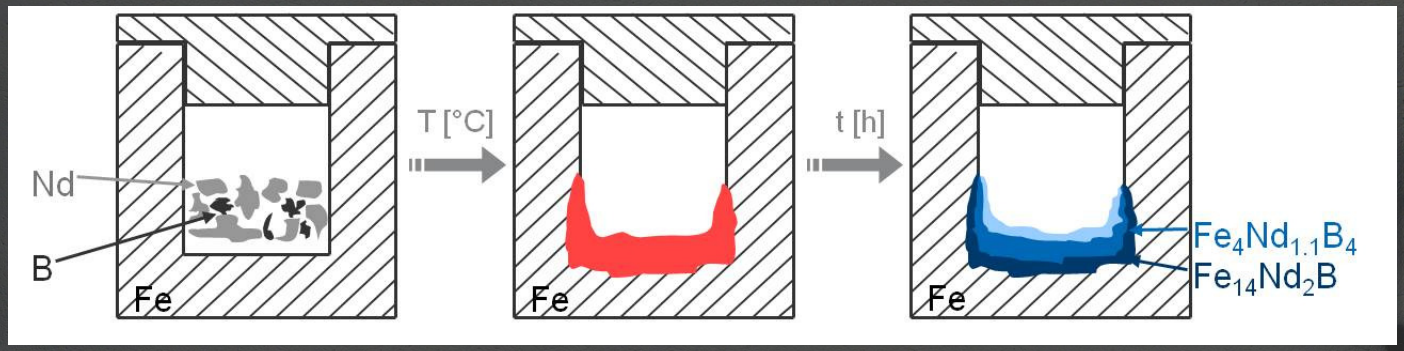
Priority setting (index)

- Non toxic
- Cost efficient/ available
- Probability to form intermediate phases
- Physical principles

Search for new magnetic phases criteria for efficient synthesis

- High probability to receive numerous phases (e.g. stable and metastable)
  - Non-equilibrium states in binary and higher component systems
- Interest focused on TM-rich phases
- Small specimen
- Quick and easy process
- Grain size of new phases should be larger than 10 µm (due to analysis method)

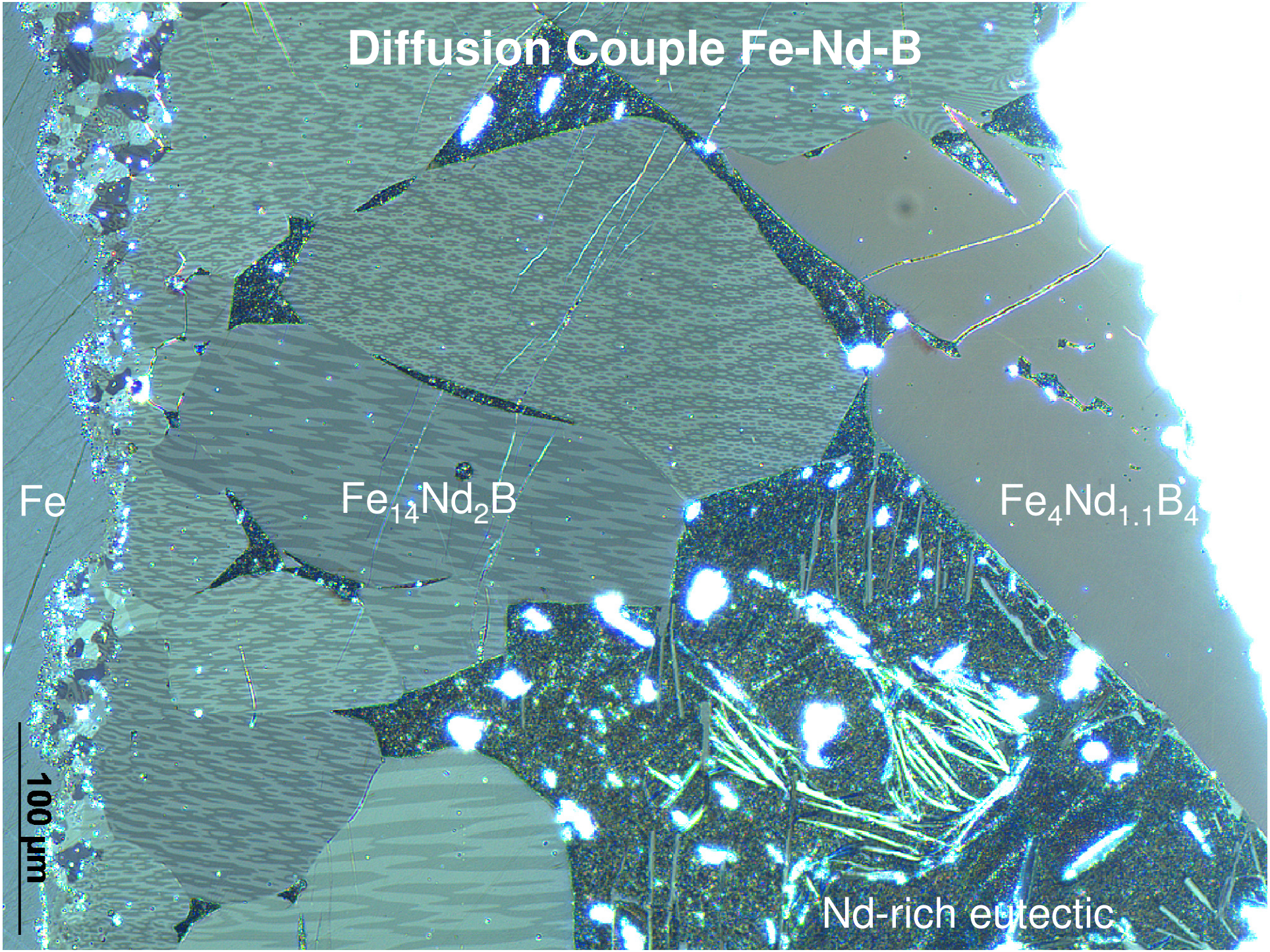
Diffusion Couple Fe-Nd-B



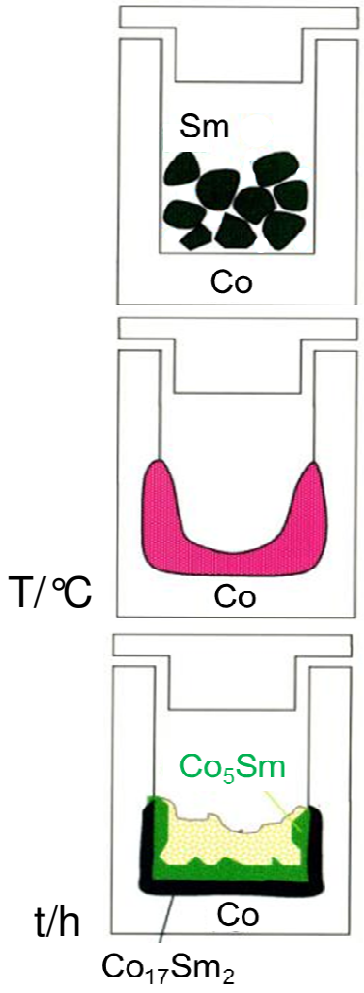
The intermetallic phases form during isothermal annealing and during cooling

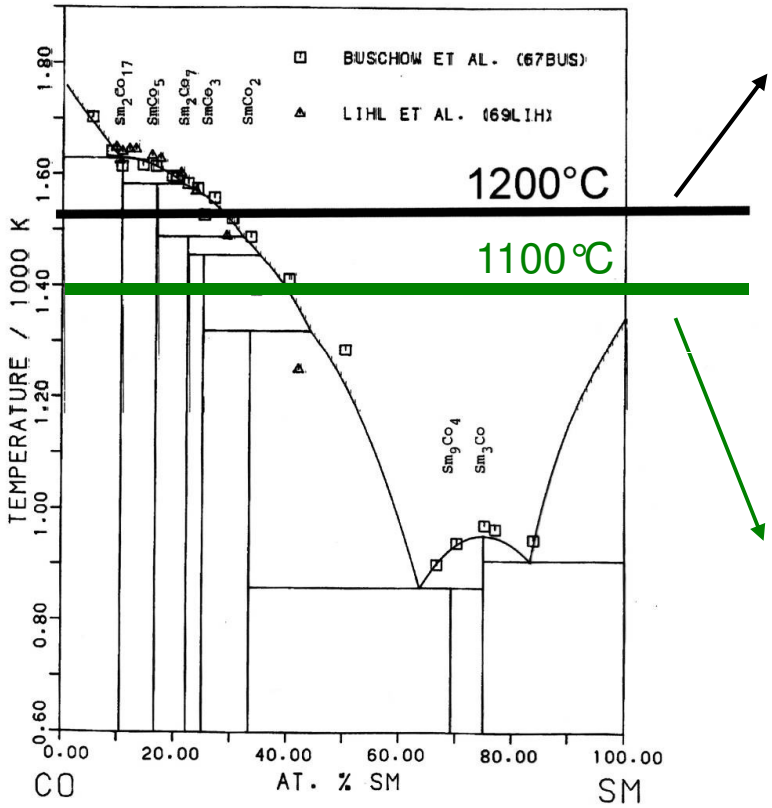
2000 µm

100 µm

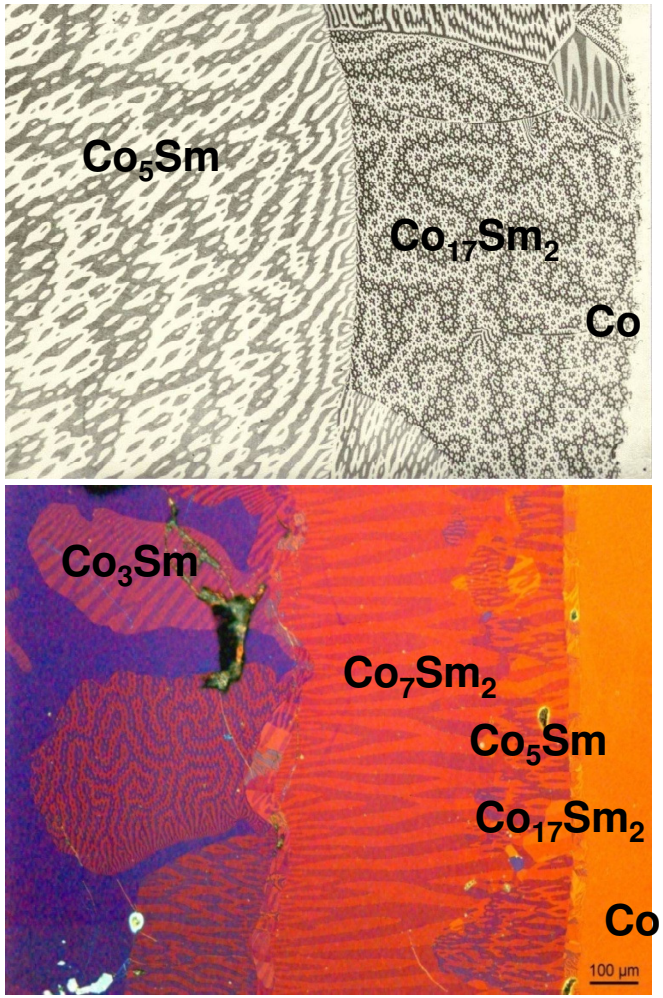

Diffusion Couple Fe-Nd-B
Fe
$Fe_{14}Nd_2B$
$Fe_4Nd_{1.1}B_4$
Nd-rich eutectic
100 µm

Diffusion Couple – Binary System Co-Sm

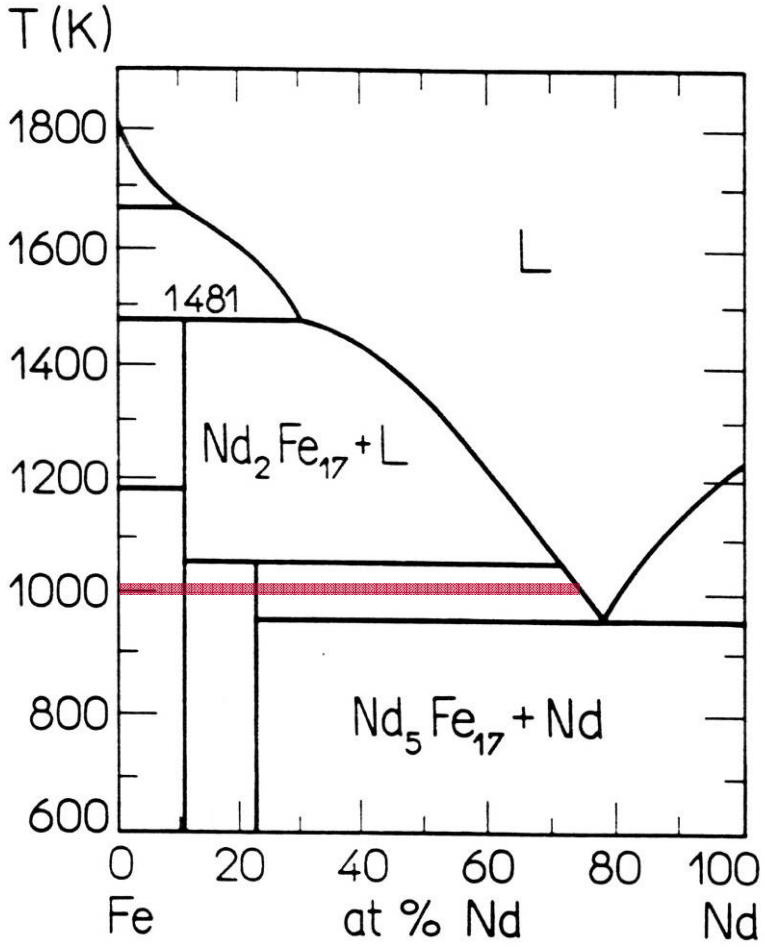




Compared to the phase diagram all phases are found in the diffusion couple



Diffusion Couple – Binary System Fe-Nd



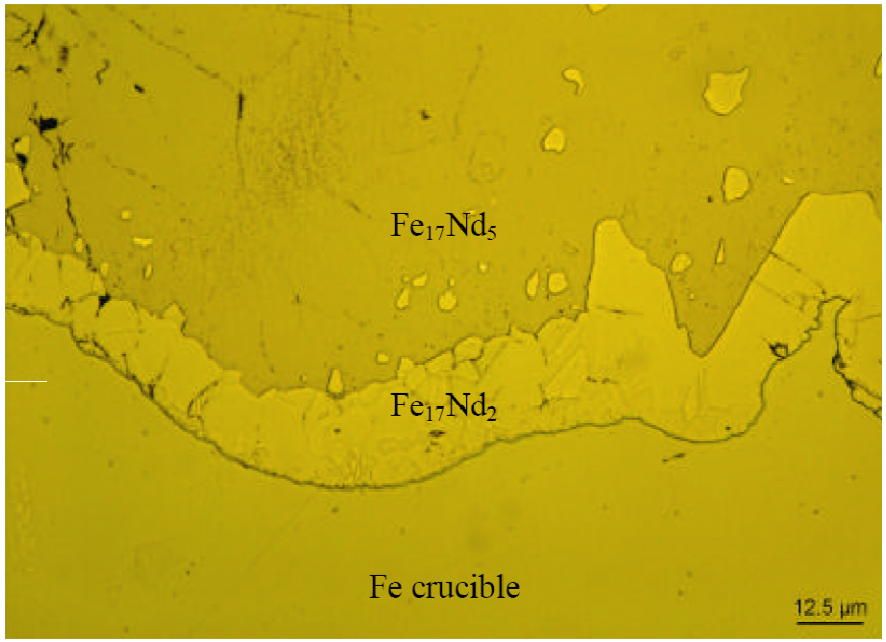
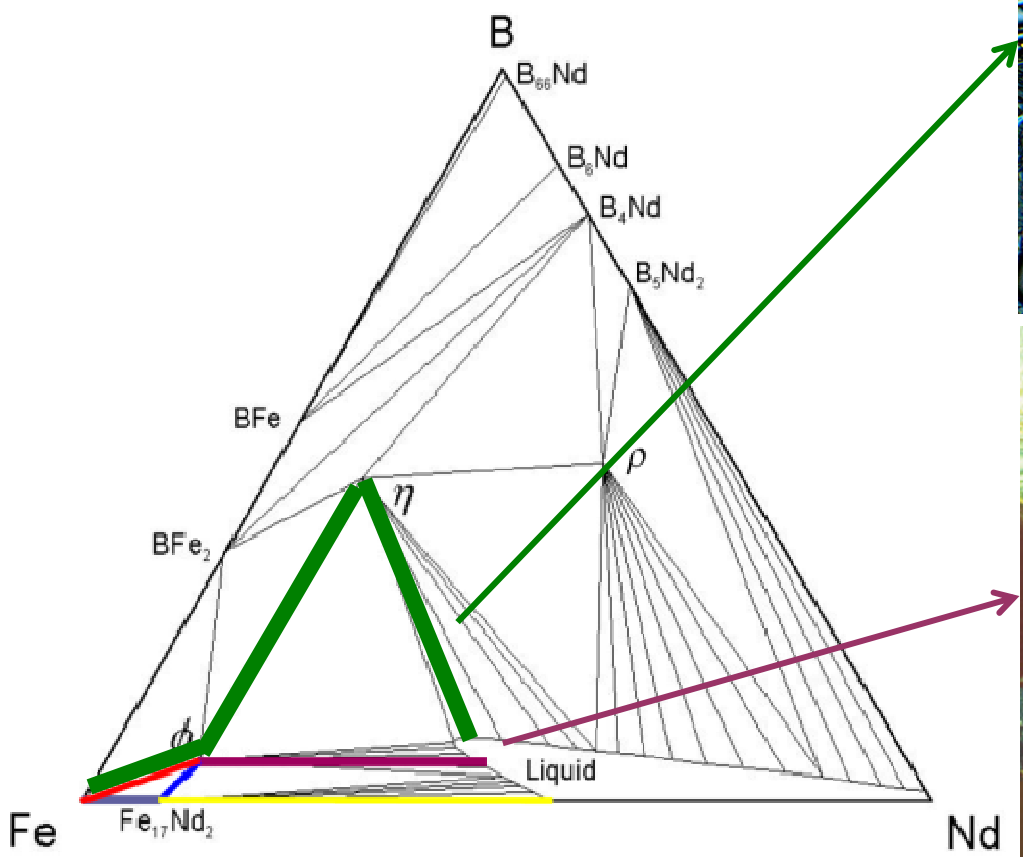
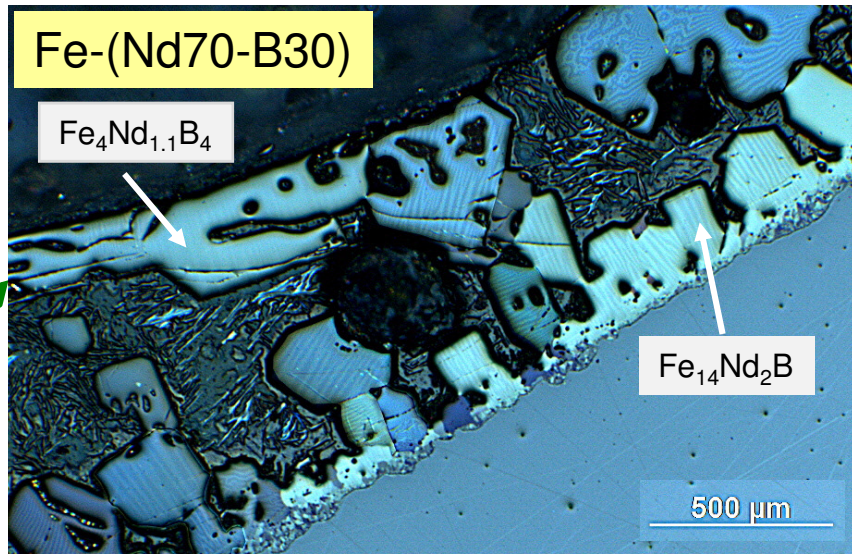
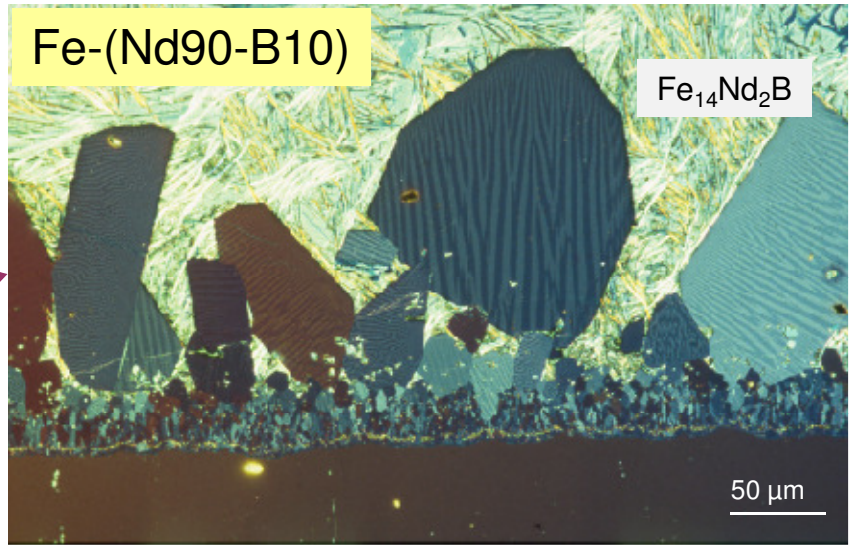


Figure 6.5: Bright field micrograph of an Fe-(Nd100) diffusion couple after a 1050°C heat treatment for 10 hours and 725°C for 30 days. For a better separation between the iron crucible (bottom), the $Fe_{17}Nd_2$ phase (middle) and the $Fe_{17}Nd_5$ phase (top) the specimen was etched with Nital.

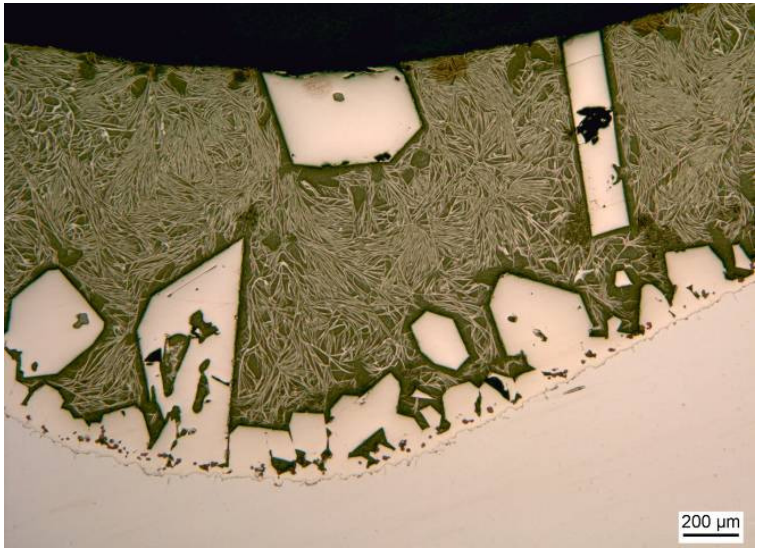
Diffusion Couple – Ternary System Fe-(Nd-B)

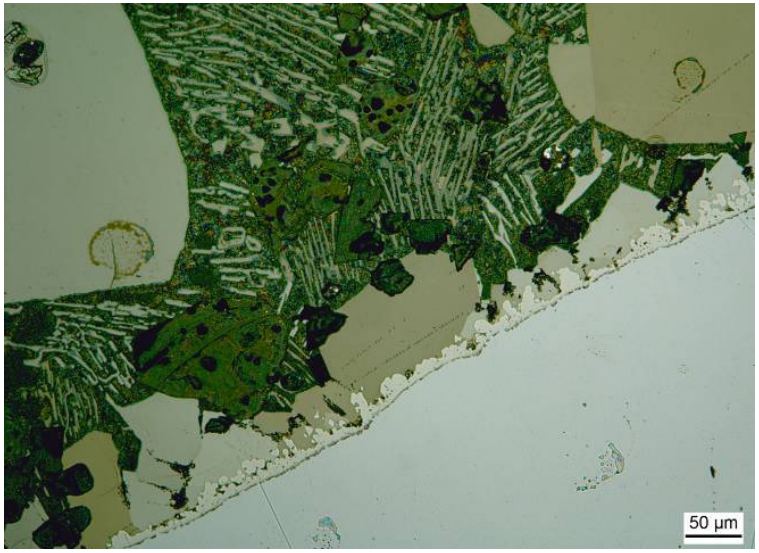


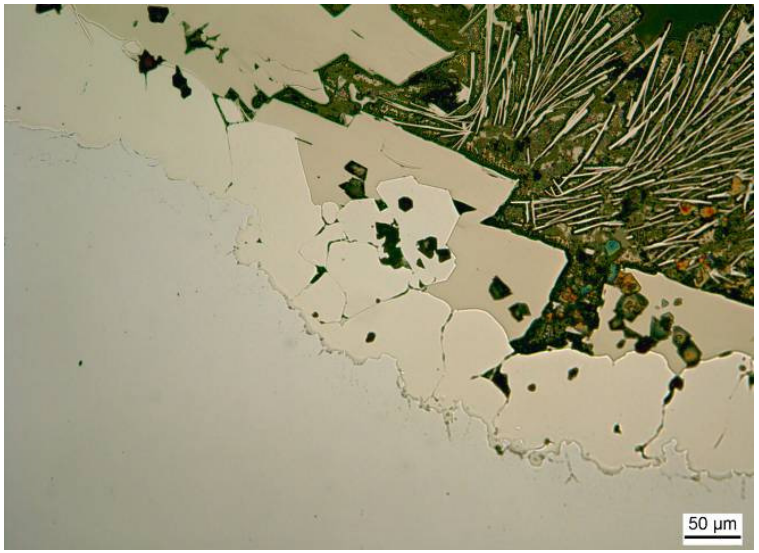




Examples of Diffusion Couples – 400 in total







Efficient analysis: Search for new magnetic phases

- High-throughput
- Determination of the intrinsic magnetic properties
- Characterization of intrinsic properties in small crystals (J_S, K_1, T_C)

Optical microscope
Phases

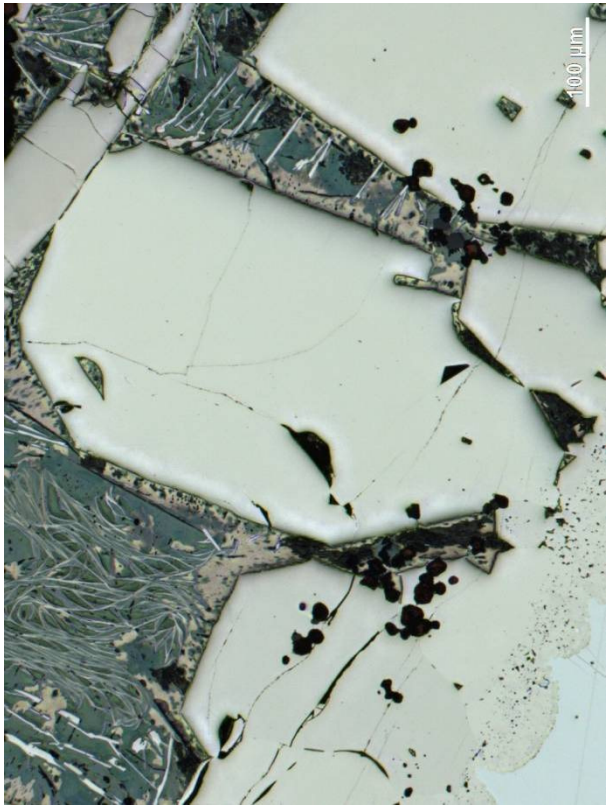
Kerr microscope
Magnetic phases

Electron microscope
Chem. composition

Efficient analysis: Search for new magnetic phases

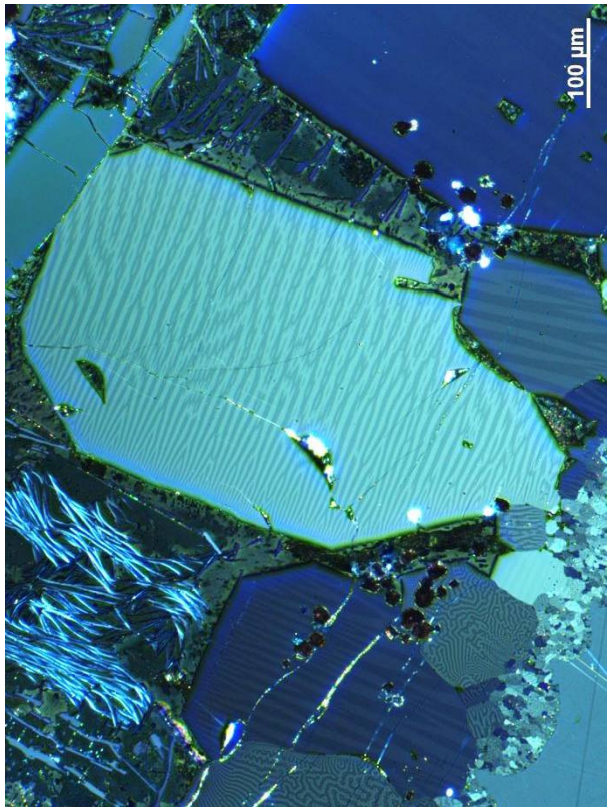
- Correlative microscopy, quantitative microstructure analysis (QMA)

Optical microscopy



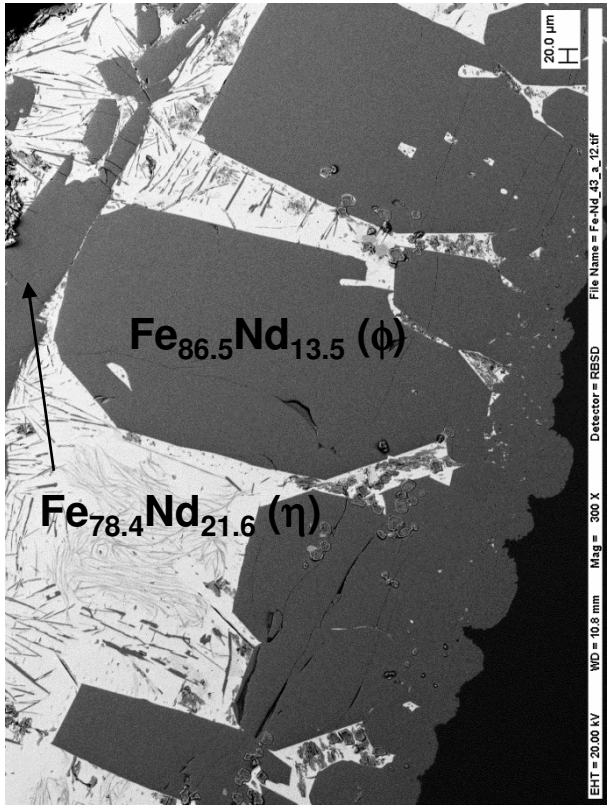
Identification of different phases

Kerr microscopy



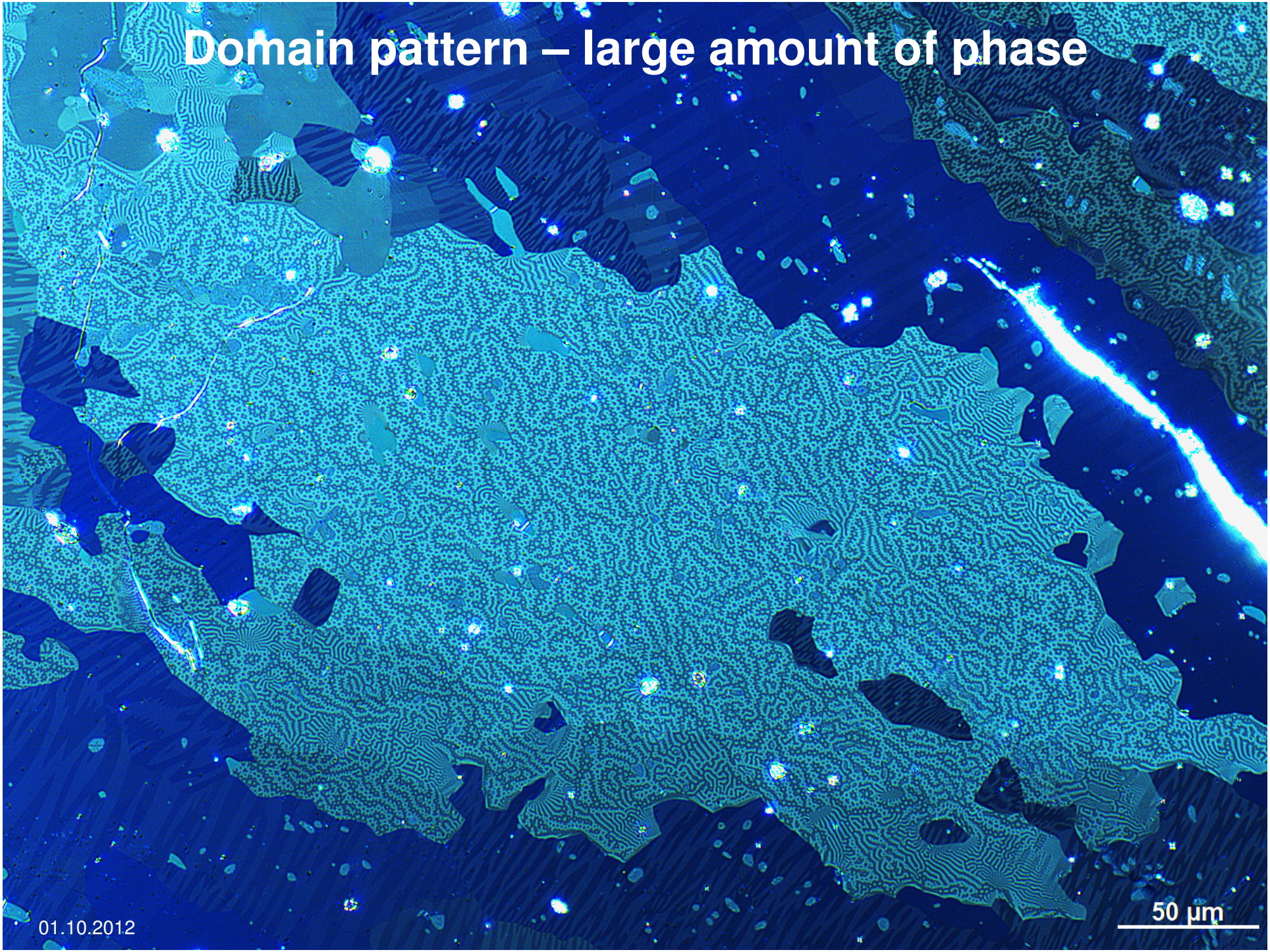
Identification of magnetic phases

REM / EDX

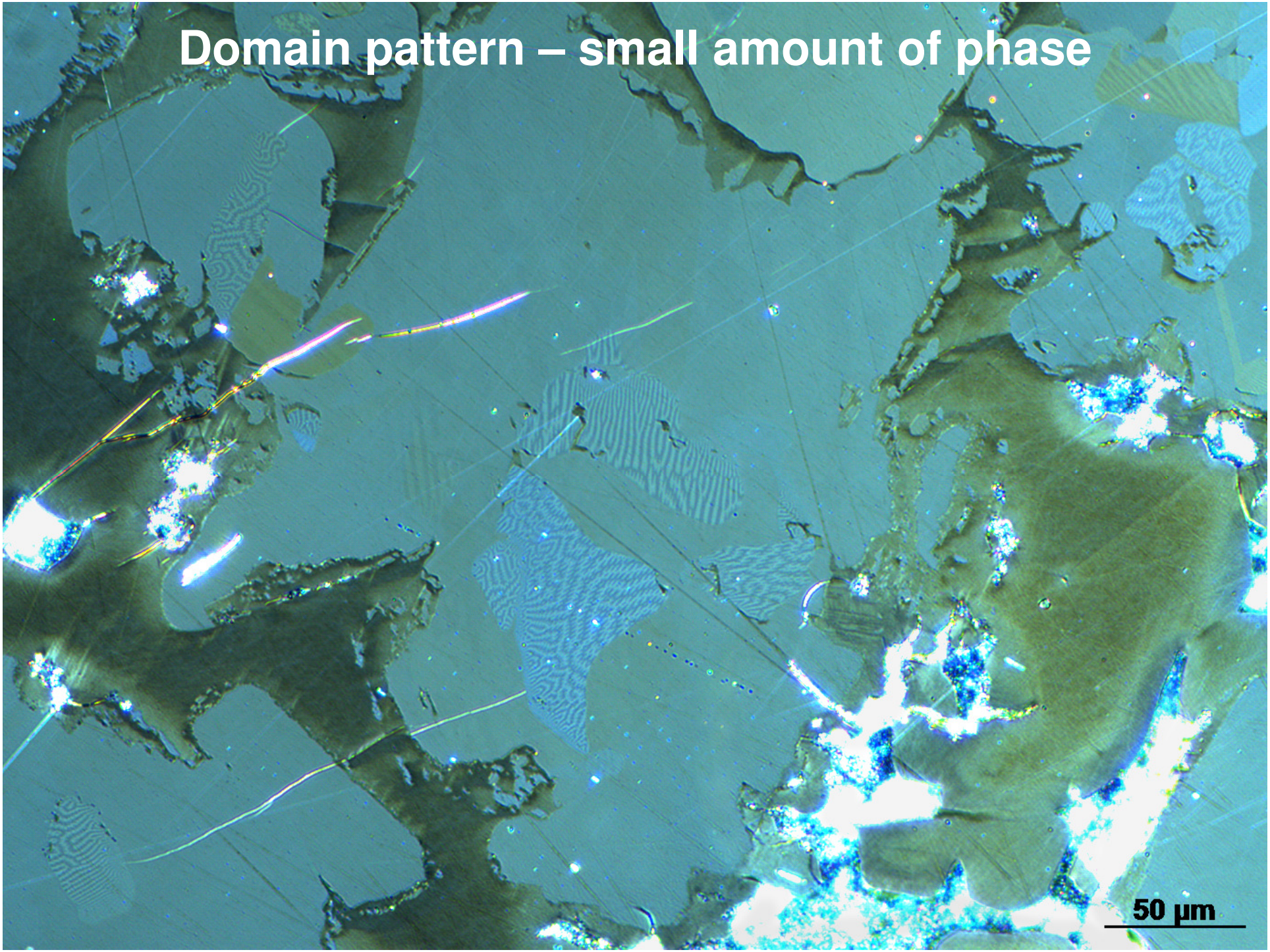


Determination of the chemical composition

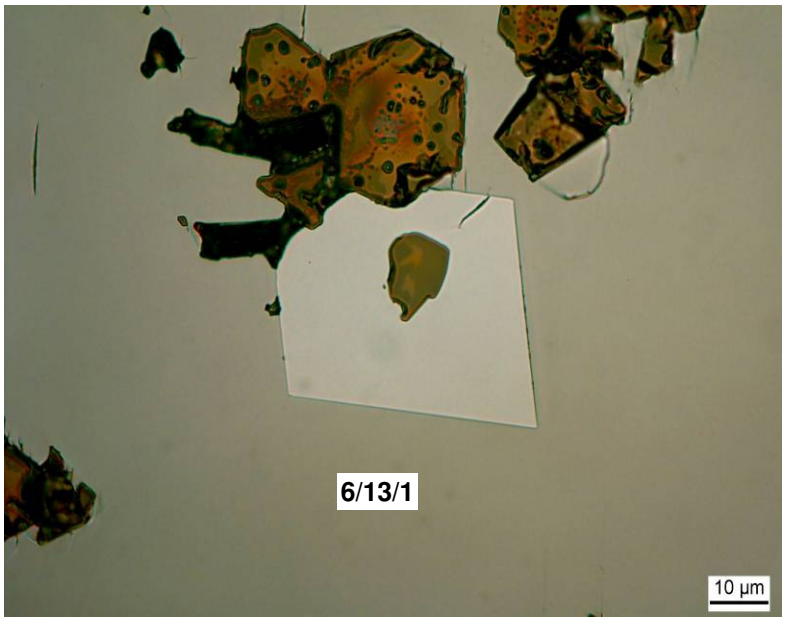
Domain pattern – large amount of phase



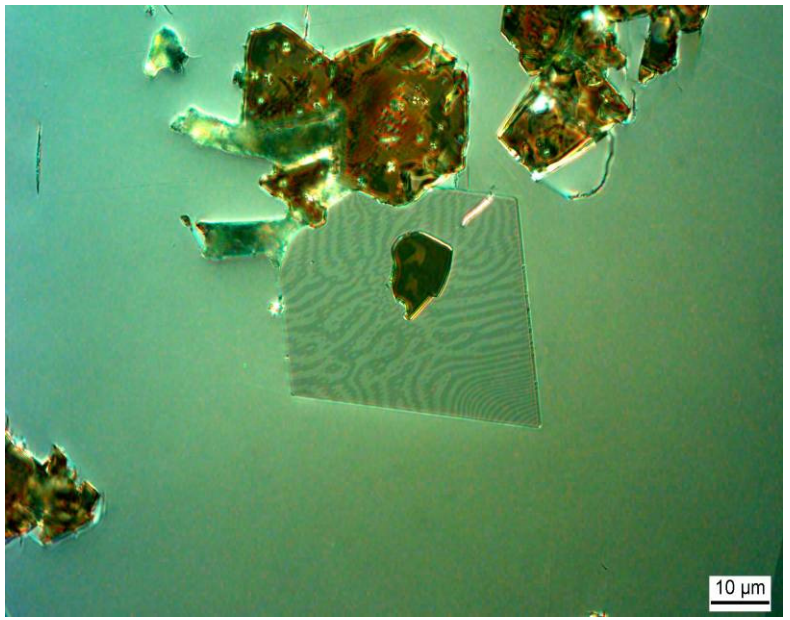
Domain pattern – small amount of phase



Ternary Fe-Pr-Mn-System

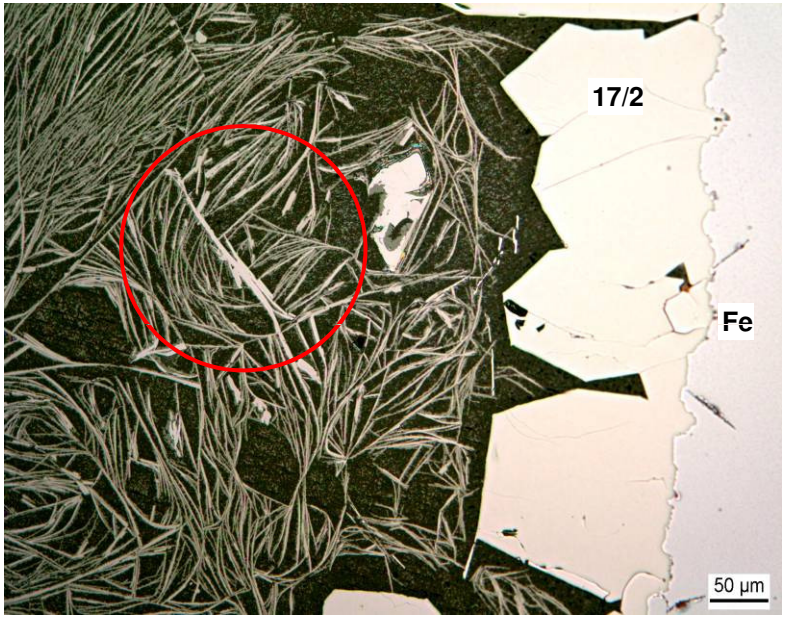


Photomicrograph of an unknown crystal surrounded by the 6/13/1 phase.

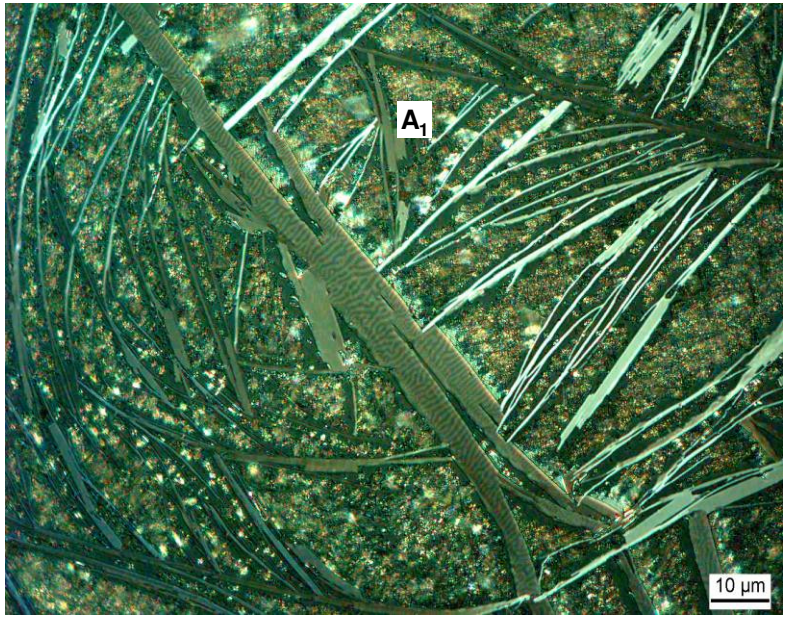


Optical micrograph in polarized light of the unknown crystal with uniaxial domain structure

Diffusion Couple Fe-(Pr90-Na10) Heat Treated at 1050 °C / 10h



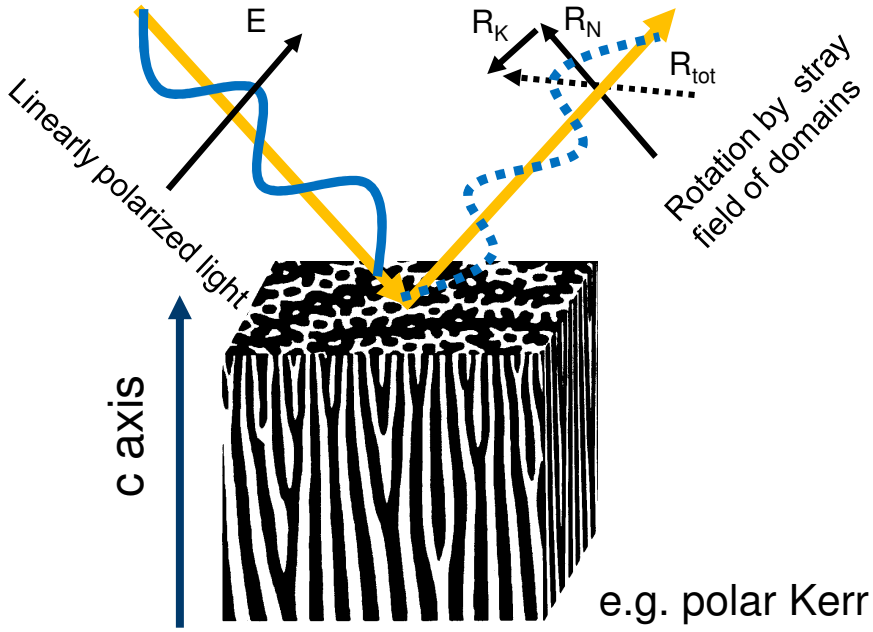
Optical micrograph of the 17/2 phase and the eutectic.



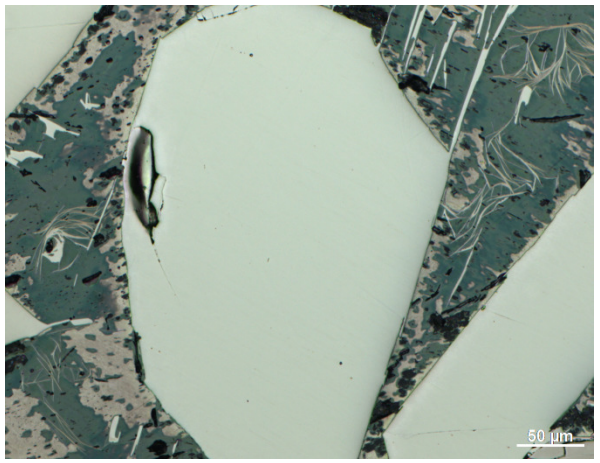
Optical micrograph in polarized light of the A_1 phase with domain pattern.

Kerr effect using the example of $Nd_2Fe_{14}B$

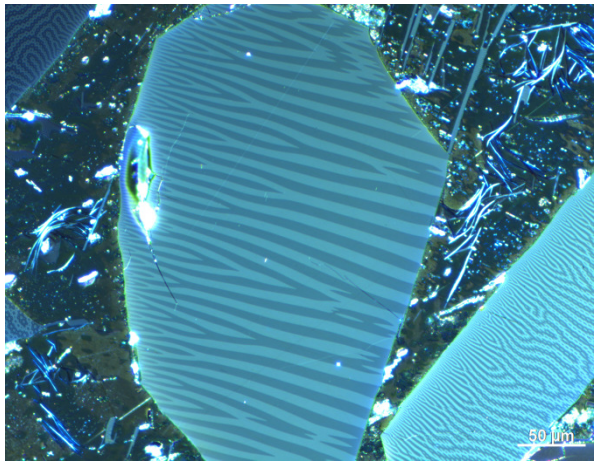
- Linearly polarized light
- Magnetic field rotates plane of polarization ($R_{tot} = R_N + R_K$)
- Visualization of domains by analysator
- Domain contrast depending on magnetization



e.g. polar Kerr effect

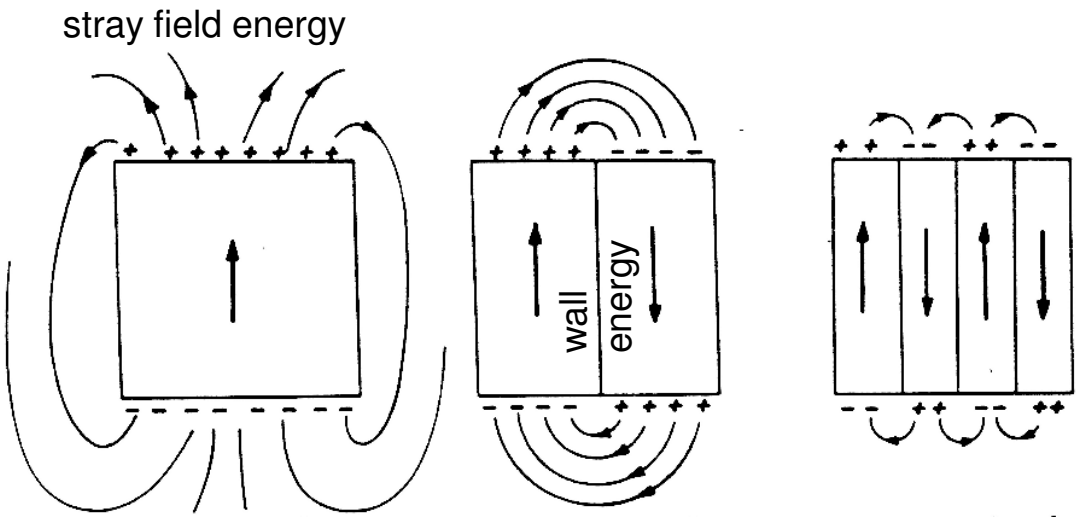


Bright field image, 200x

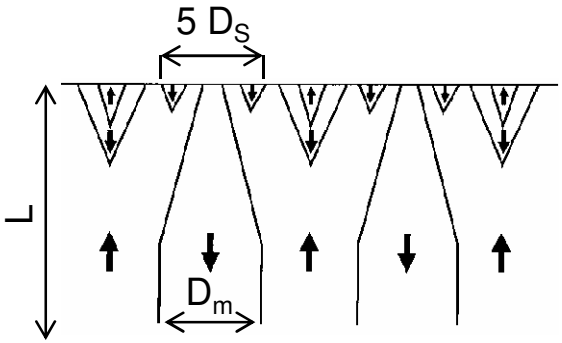


Kerr image, 200x

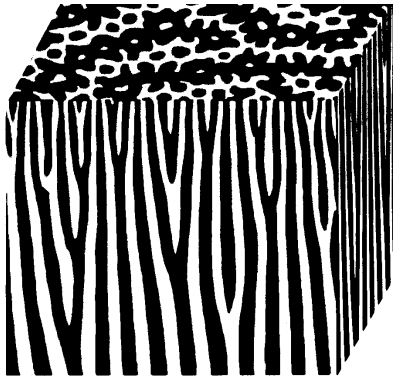
Domain pattern for uniaxial anisotropy ($Nd_2Fe_{14}B$)



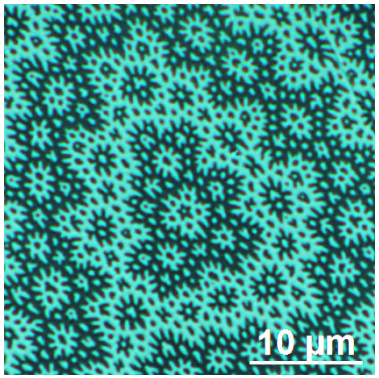
Minimization stray field energy by reversed spikes



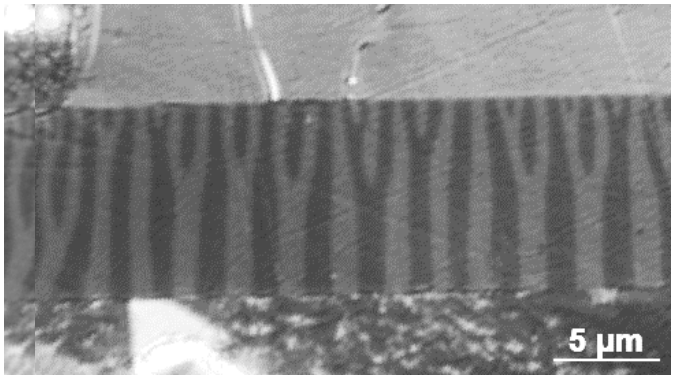
D_m: domain width
L : grain thickness



3D-model

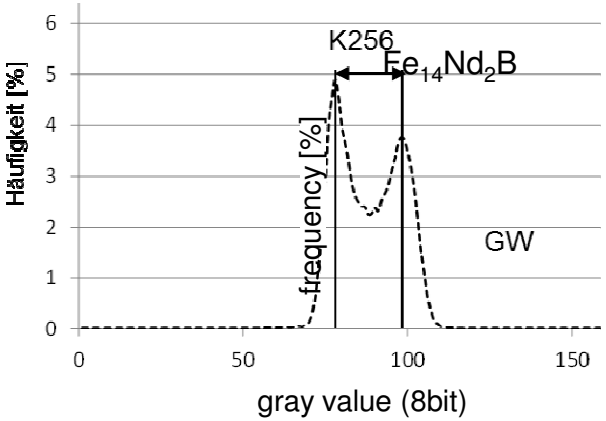


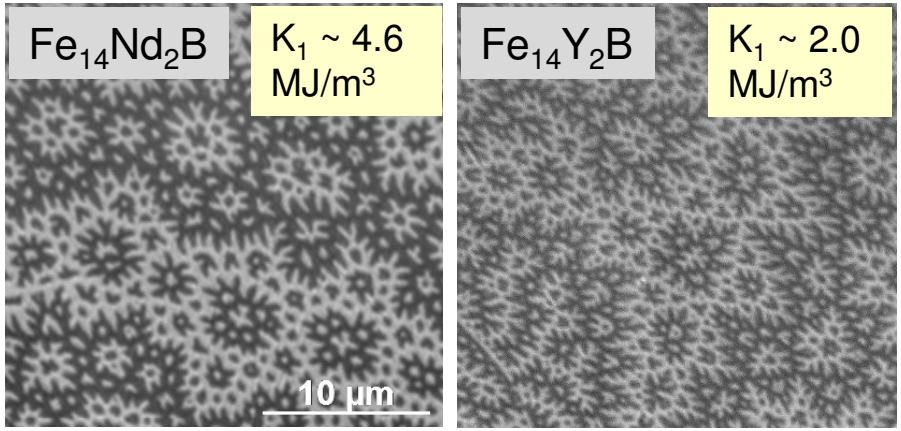
closure domain with reversed spikes

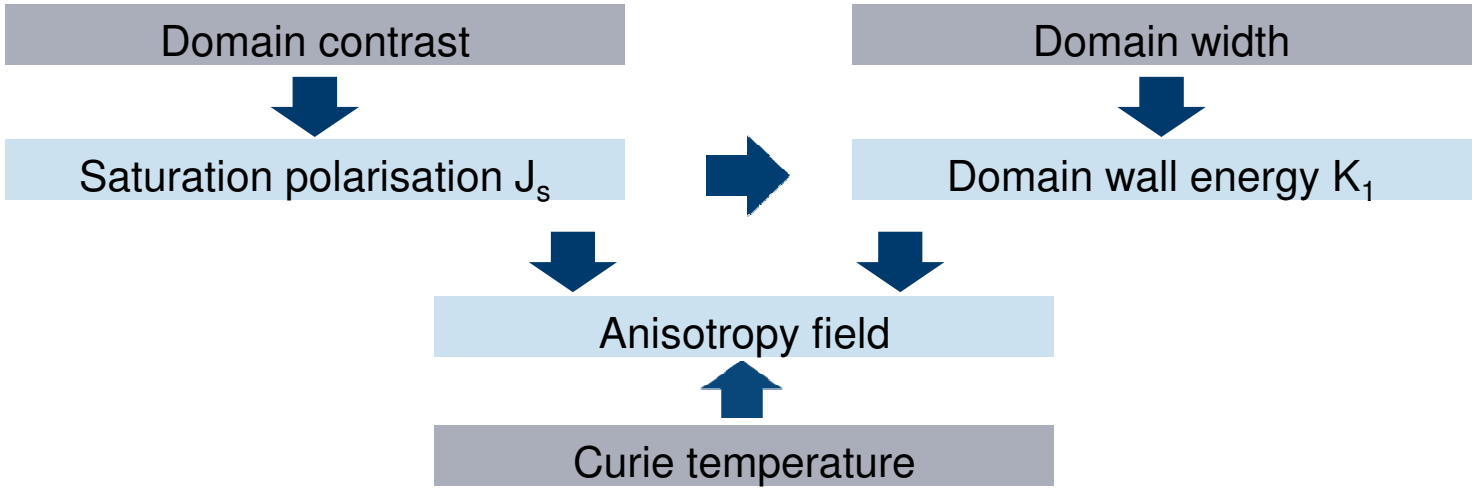


stripe domain with branching

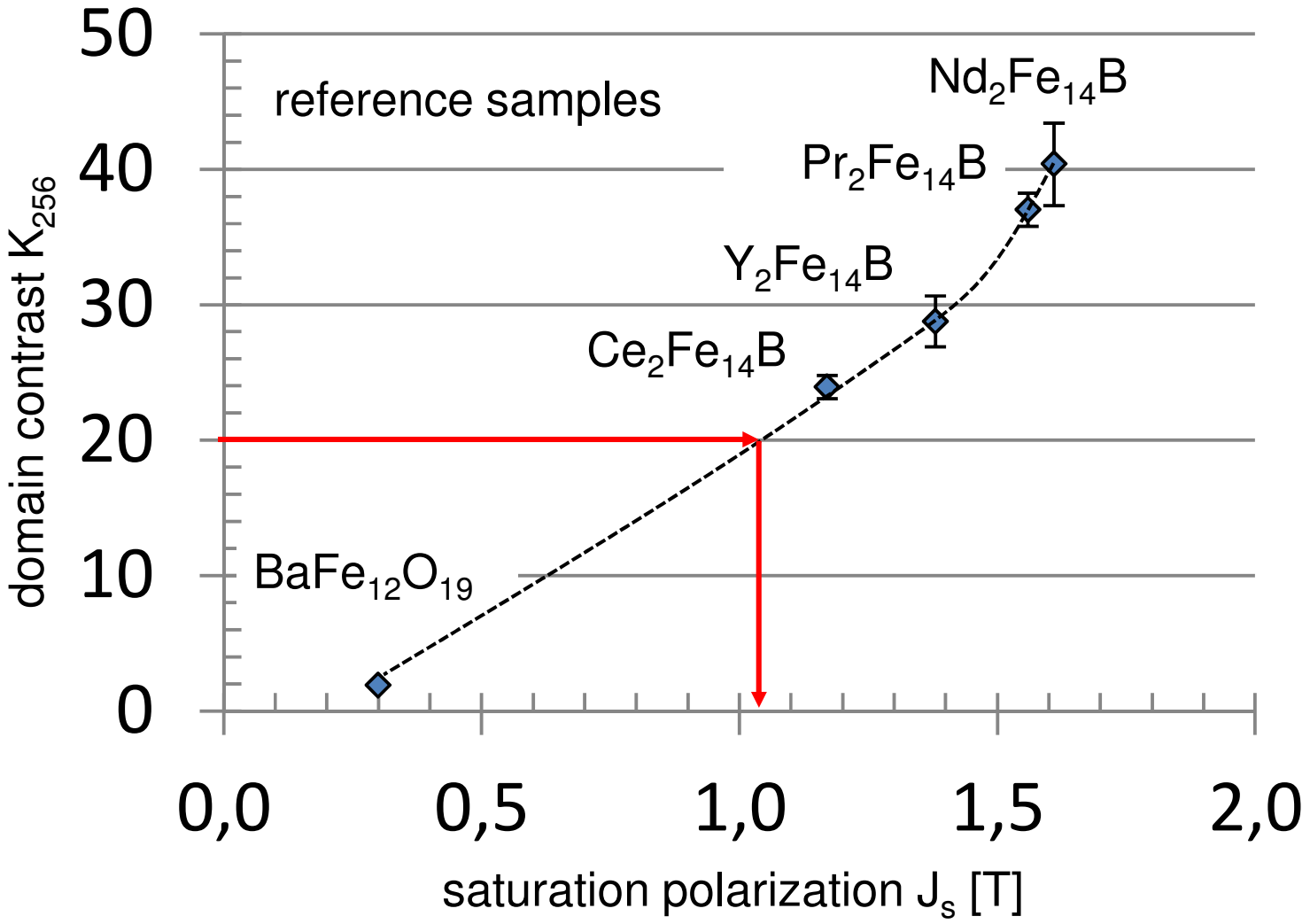
Relationship between domain pattern and intrinsic magnetic properties

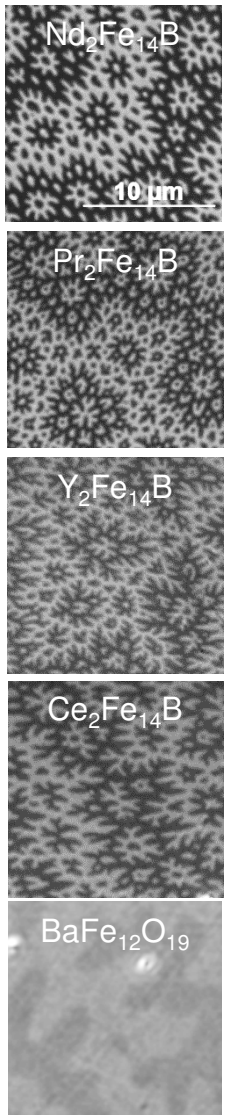






Saturation polarization J_S from domain contrast





Anisotropy constant K_1 from domain width

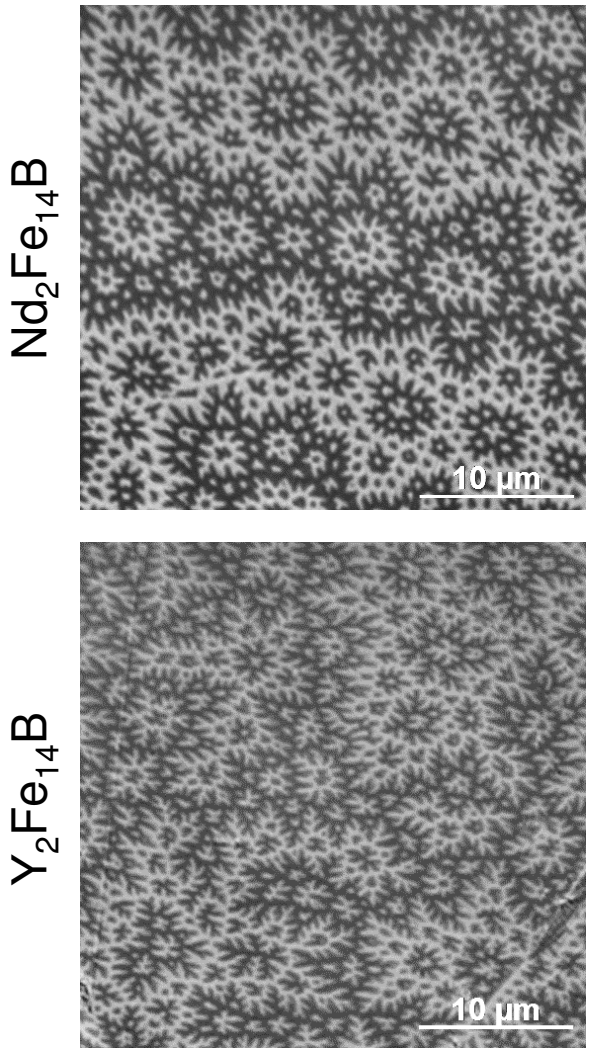
- Different models for determination of K_1

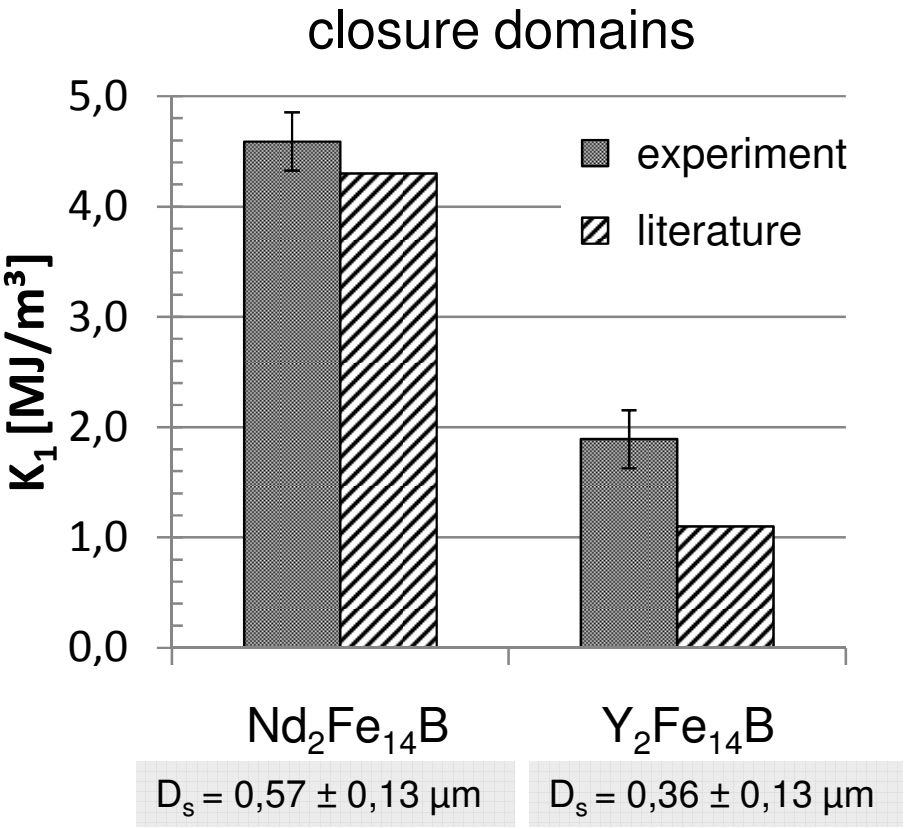
Domain pattern	Formula	Reference
stripe domain for grain thickness < 10 µm	$D_m = (\gamma L/1.7M_S^2)^{1/2}$	[Kit46] C. Kittel, Phys. Rev. 70, 965 (1946)
stripe domain, for grain thickness > 10 µm	$D_m = 0.395(\gamma\mu^*/M_S^2)^{1/3} L^{2/3}$	[Szy73] R. Szymczak, Acta Phys. Pol. A 43, 571 (1973)
closure domain, for grain thickness > 80 µm	$D_s = \beta 4\pi\gamma/M_S^2$	[Bod77] R. Bodenberger, A. Hubert, Phys. Stat. Sol. (a) 44, K7-K11 (1977)

- Wall energy $\gamma = 4(AK_1)^{1/2}$, with exchange constant $A \approx 1*10^{-11}$ J/m

- For identical grain thickness phases with larger magnetocrystalline anisotropy show a larger domain width compared to phases with smaller anisotropy constant.

Anisotropy constant K_1 from domain width

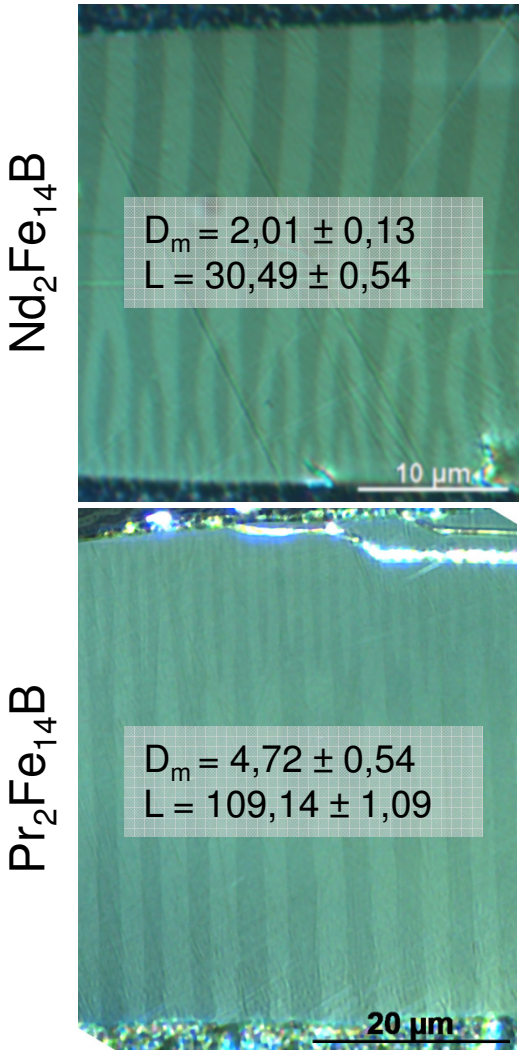


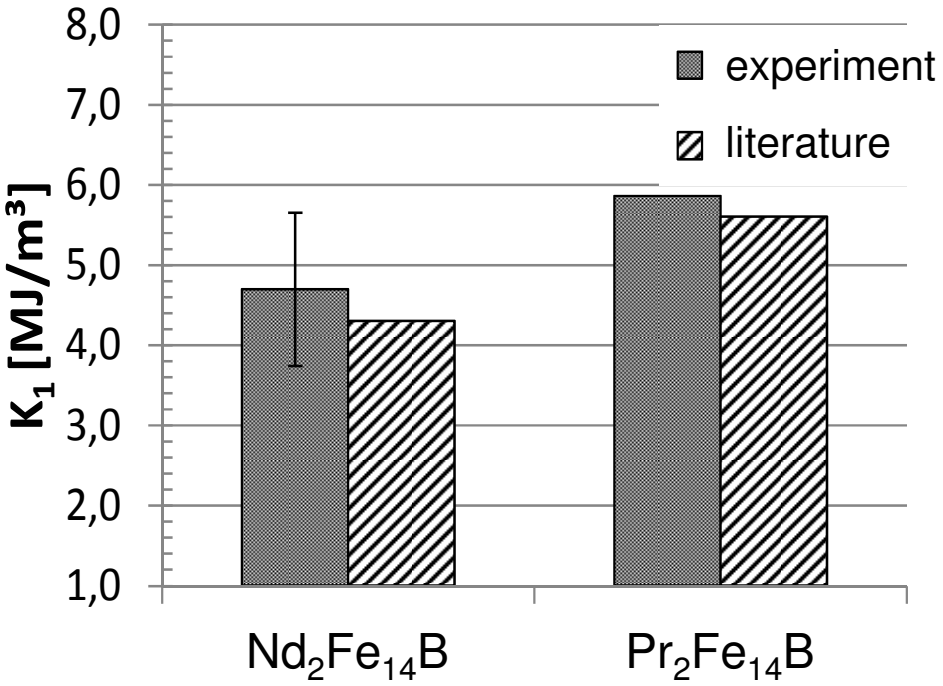


$D_s = \beta 4\pi\gamma / M_s^2$ [Bod77] ($\beta = 0.31$)

Kerr images, 1000x, oil pole

Anisotropy constant K_1 from domain width



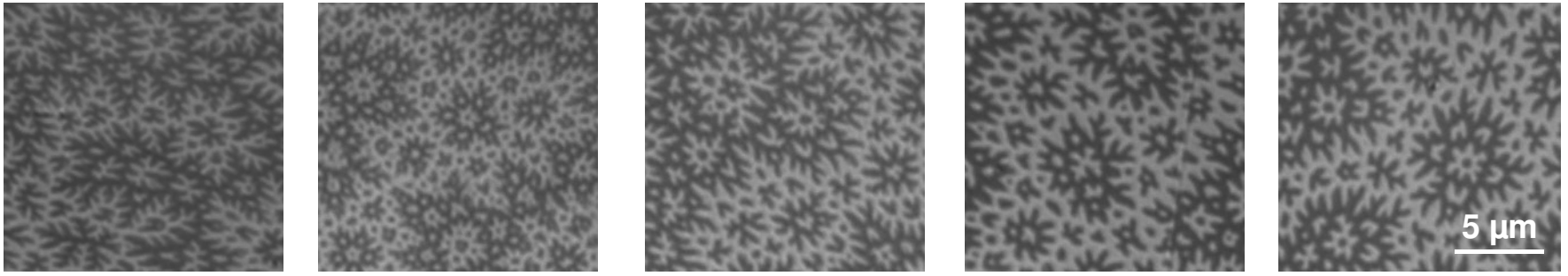


$$D_m = 0.395(\gamma\mu^*/M_S^2)^{1/3} L^{2/3}$$ [Szy73]

Average grain thickness: L [µm]
Average domain width: D_m [µm]

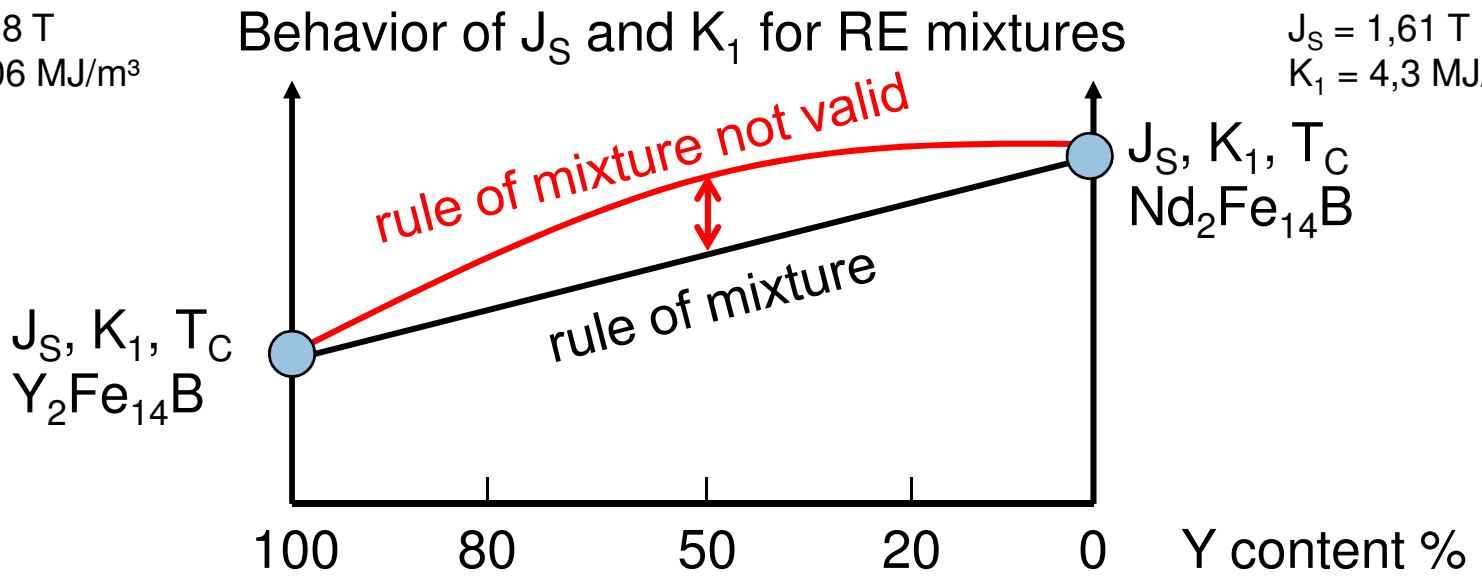
Kerr image, 500x und 1000x oil pole

Example $(Y_{1-x}Nd_x)_2Fe_{14}B$ (x = 0..1)



$Y_2Fe_{14}B$ $Y_{1.7}Nd_{0.3}Fe_{14}B$ $Y_{1.0}Nd_{1.0}Fe_{14}B$ $Y_{0.3}Nd_{1.7}Fe_{14}B$ $Nd_2Fe_{14}B$

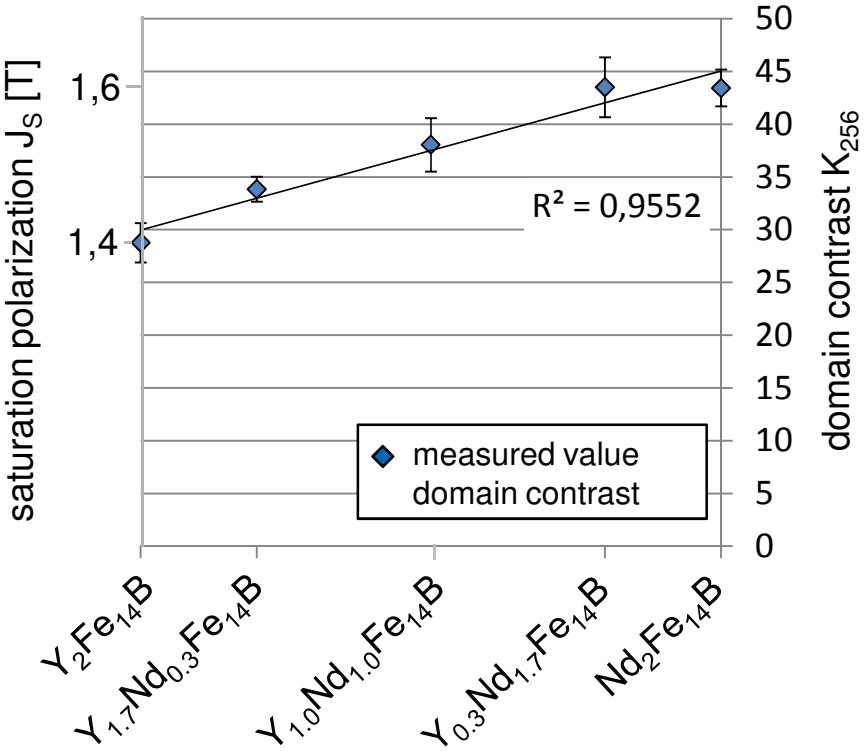
J_S = 1,38 T
K_1 = 1,06 MJ/m³



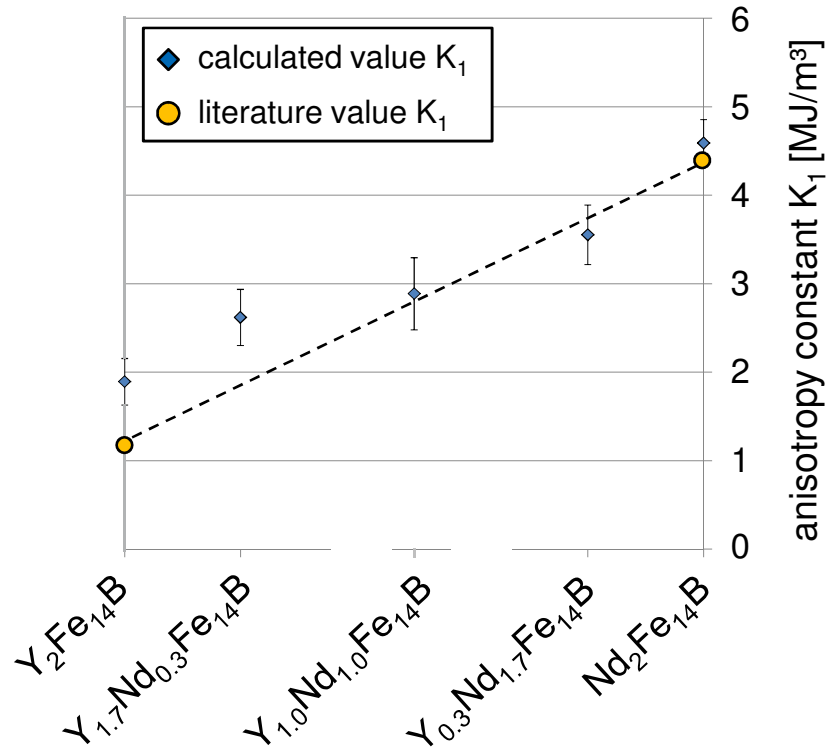
J_S = 1,61 T
K_1 = 4,3 MJ/m³

Example $(Y_{1-x}Nd_x)_2Fe_{14}B$ (x = 0..1)

- J_s and K_1 as function of ratio Y:Nd



Estimation saturation polarization J_s based on measured domain contrast



Estimation anisotropy constant K_1 based on measured domain surface width

Search for new permanent magnetic materials

- High Throughput synthesis and analysis methods established
- Search in about 400 different systems completed
- Existence of phases in TM rich corner documented, some interesting candidates identified
- *Still some work to be done!*
  - *Support by first principle approaches needed*
    - *Crystal structures, chemical composition*
    - *Thermodynamic stabilities*
    - *Magnetic properties*
  - *Collaboration with Peter Gumbsch and Ralf Drautz*
    Modeling tools still to be developed

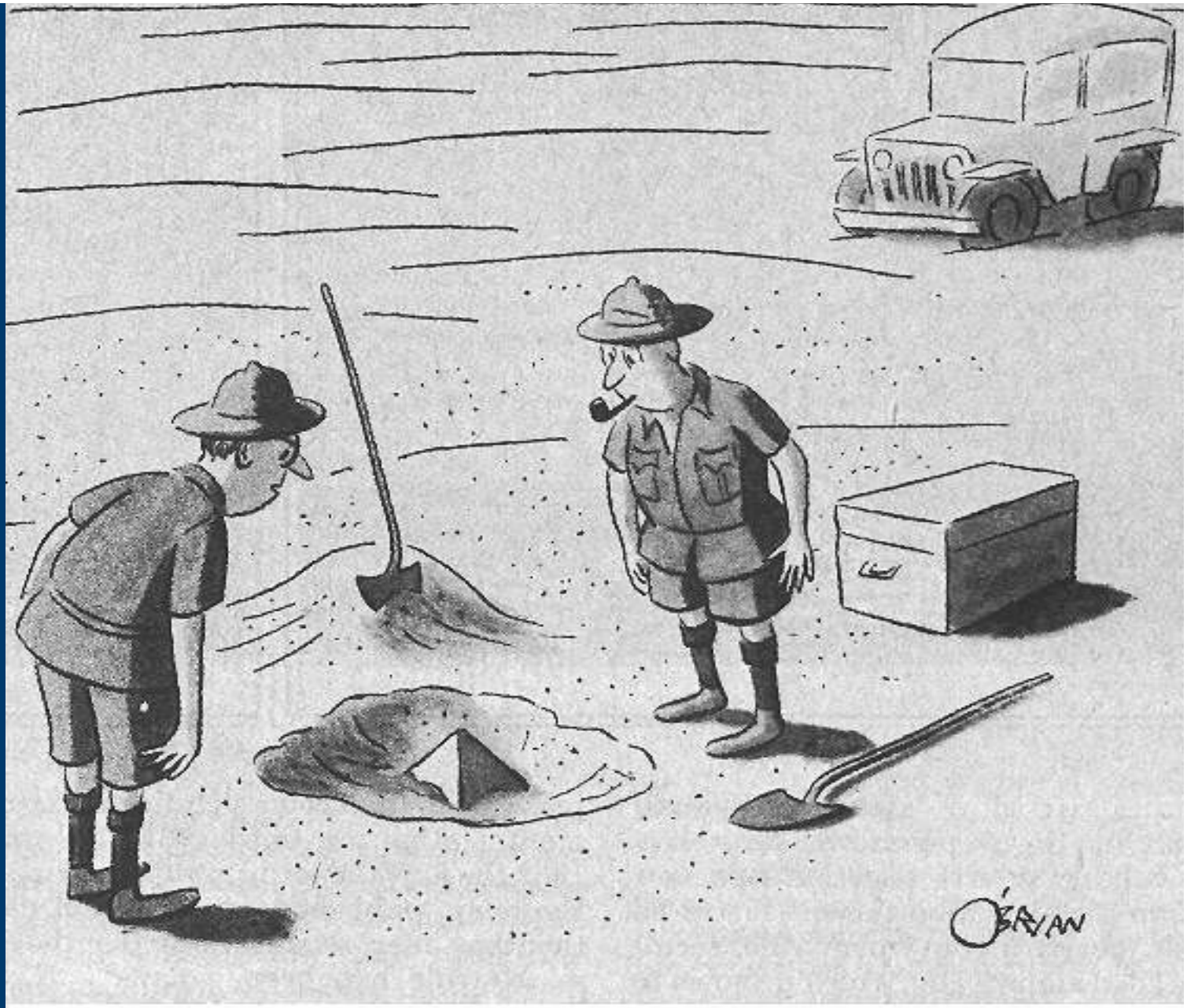
Diffusion couple	$Fe_{17}Sm_2$	Fe_3Sm	Fe_2Sm	$Fe_{12}Sm$	$Fe_{29}Sm_3$	$Fe_{14}Sm_6$
Fe-Sm-Mg	✗	✓strong	✓weak			
Fe-Sm-Ti	✗	✓strong	✓weak	✓strong		
Fe-Sm-V	✓weak	✓strong	✓weak	✓strong		
Fe-Sm-Cr	✗	✓strong	✓weak			
Fe-Sm-Mn	✗	✓strong	✓weak	missing		
Fe-Sm-Co	✓weak	✓strong	✓weak			
Fe-Sm-Ni	✗	✓strong				
Fe-Sm-Cu	✗	✓strong				
Fe-Sm-Zr	✗	✓strong	✓weak			
Fe-Sm-Nb	✗	✓strong	✓weak			
Fe-Sm-Mo	✗	✓strong	✓weak		missing	
Fe-Sm-In	✓weak	✓strong	✓weak			
Fe-Sm-Sn	✓strong		✓weak			✗
Fe-Sm-Sb	✓weak		✓weak			✗
Fe-Sm-W	✗	✓strong		missing		
Fe-Sm-Pb	✗	✗				

New phase found

Phase in larger amount synthesized and analyzed

Development of processing to realize microstructure

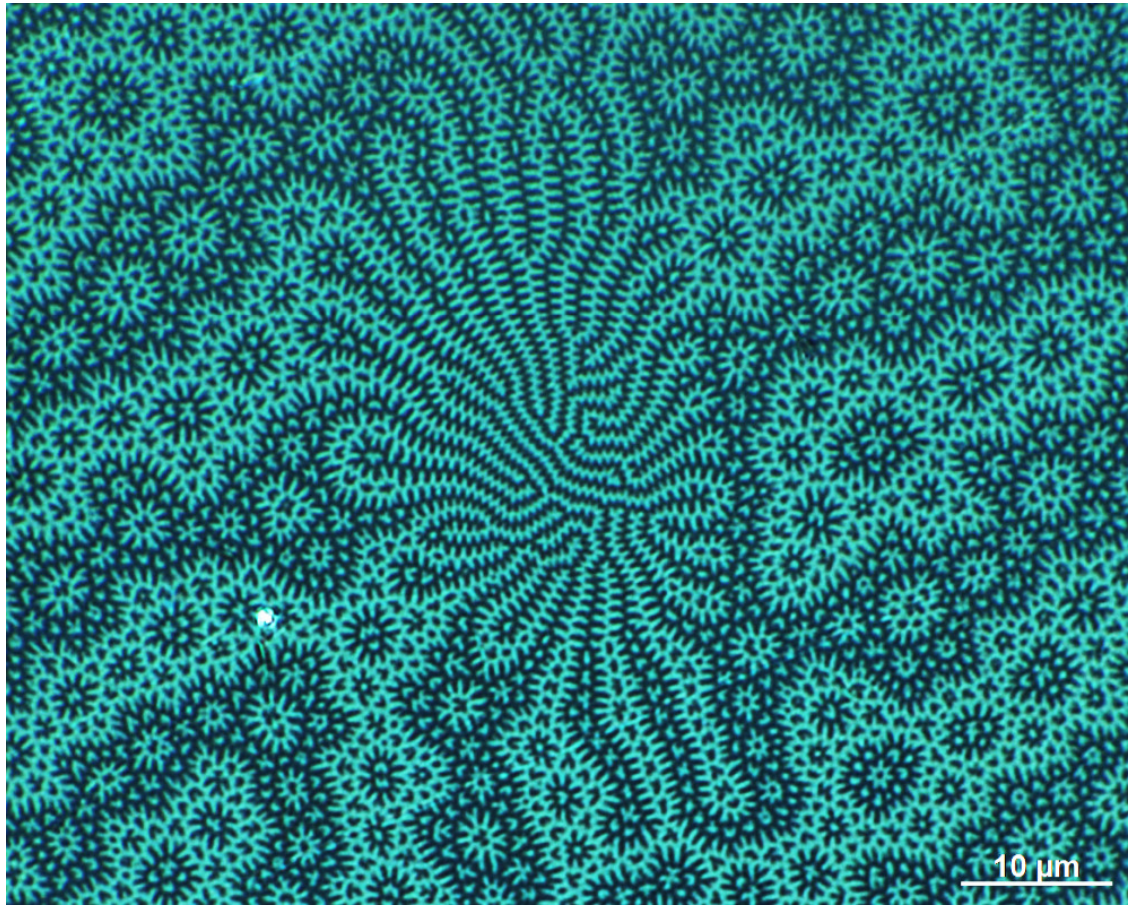
Mass production



"This could be the discovery of the century. Depending of course, on how far down it goes."

Acknowledgements

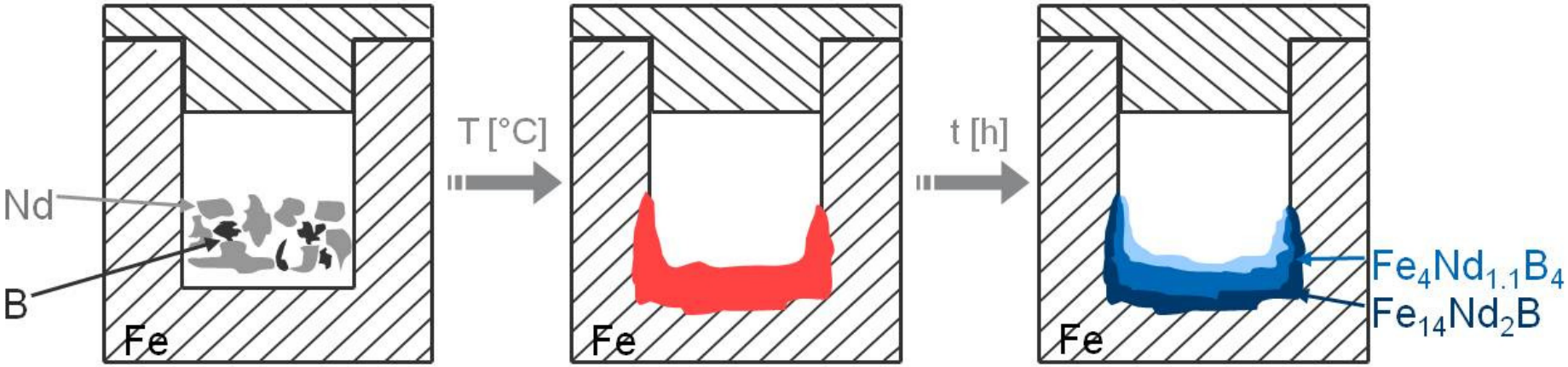
- Bundesministerium für Bildung und Forschung
- Robert Bosch GmbH
- Magnetfabrik Bonn
- Fraunhofer-Institut für Werkstoffmechanik
- Max-Planck-Institut für Intelligente Systeme



Backup

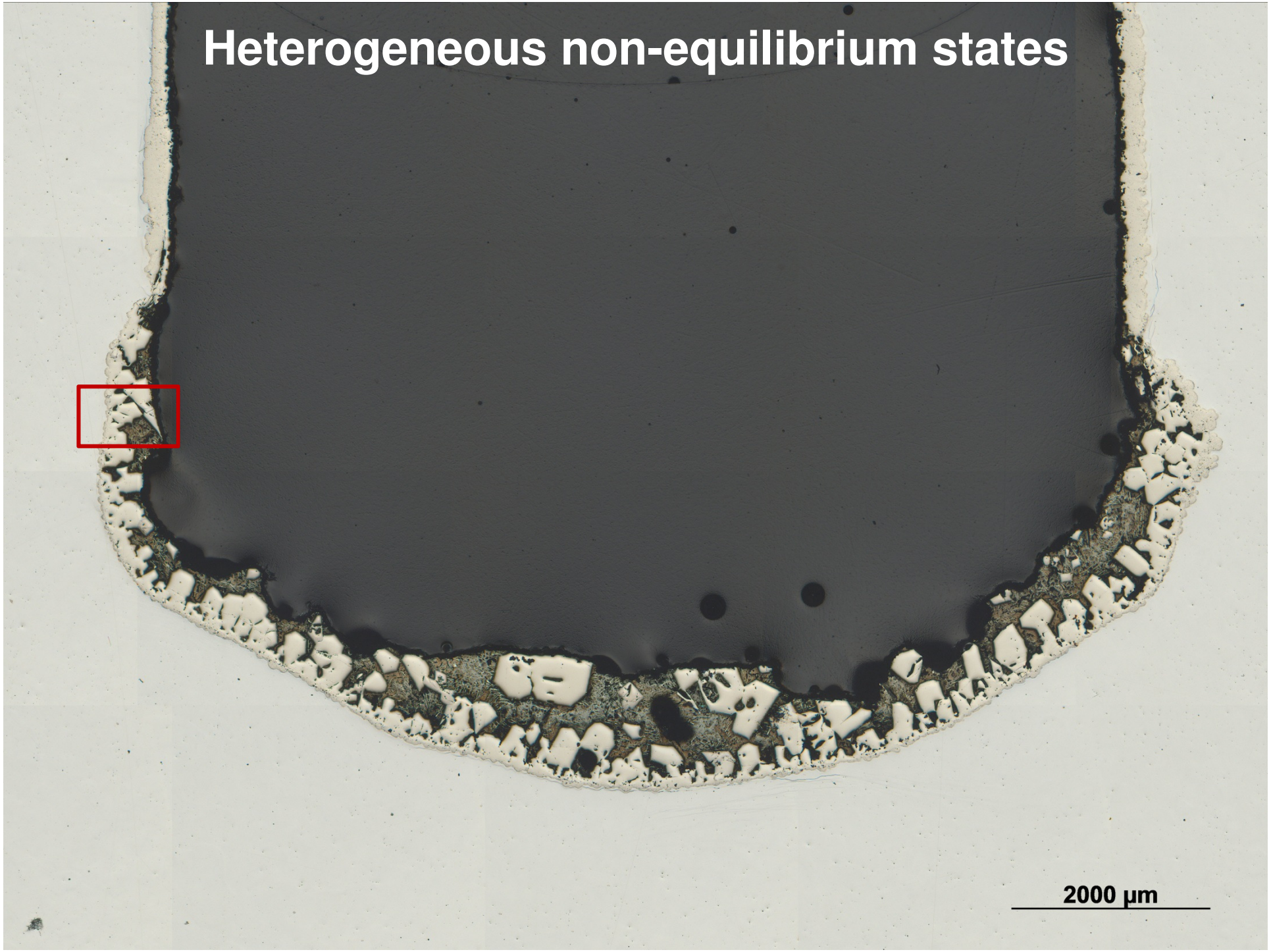
Search for new magnetic phases – efficient synthesis

- High probability to receive numerous phases
- Non-equilibrium states in binary and higher component systems
- Interest focused on TM-rich phases
- Small specimen



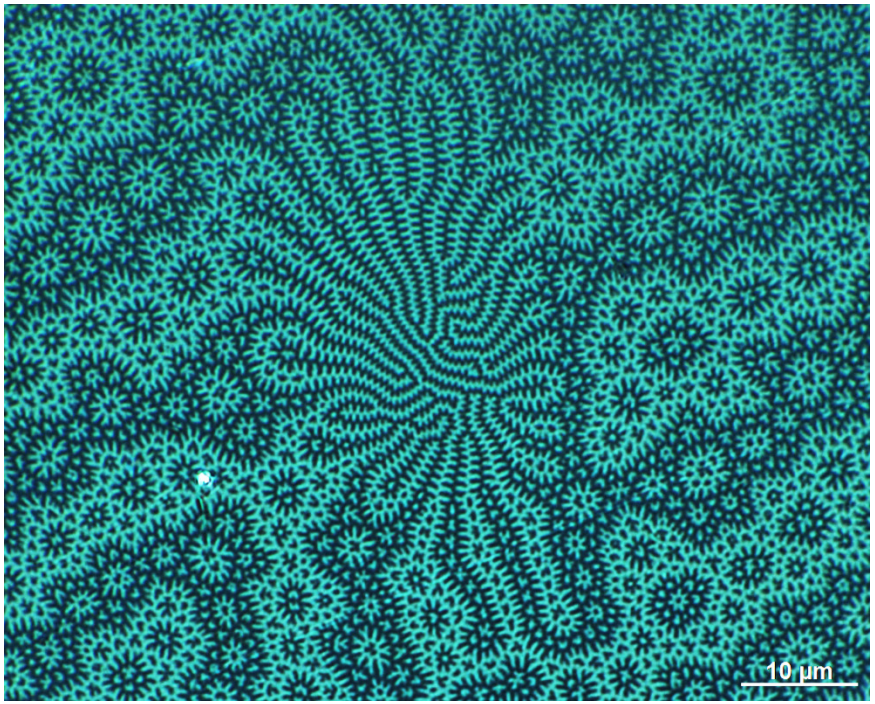
The intermetallic phases form during isothermal annealing and during cooling.

Heterogeneous non-equilibrium states

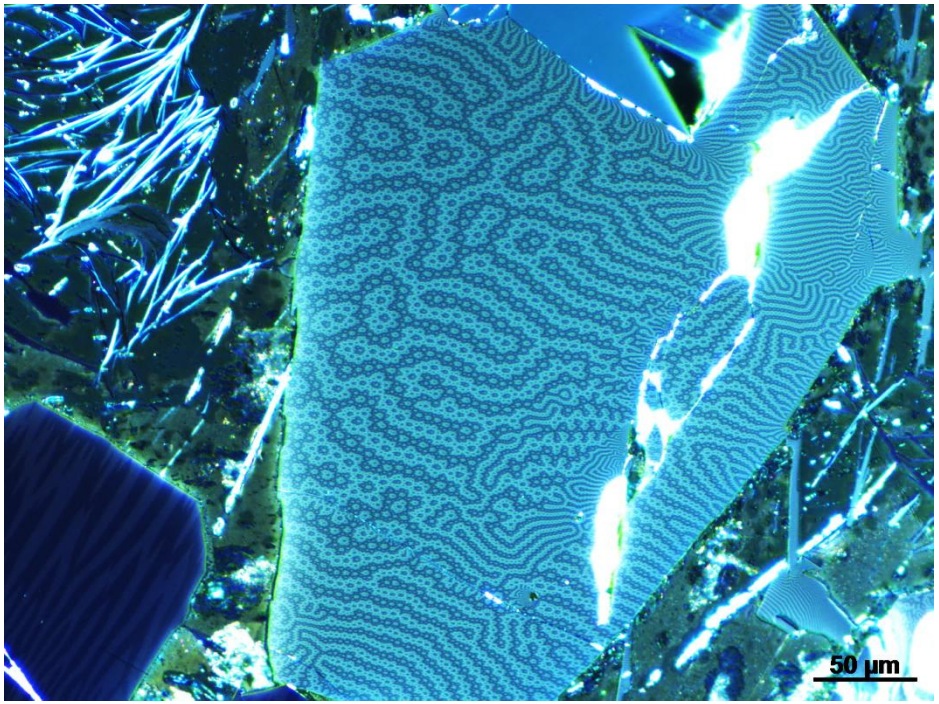


Anisotropy constant K_1 from domain width

- Dependence of domain pattern on grain thickness

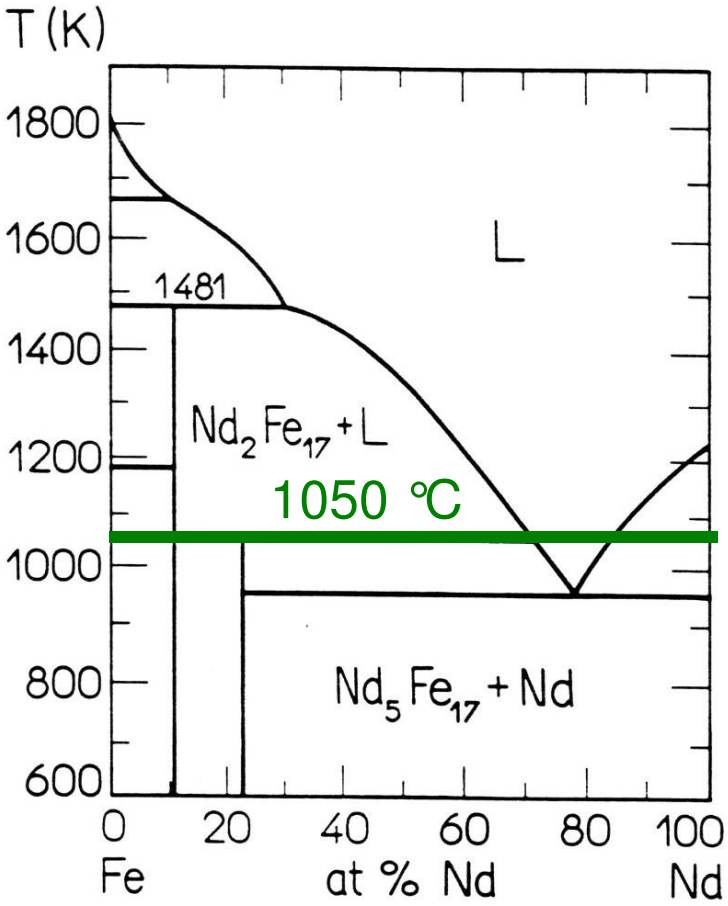


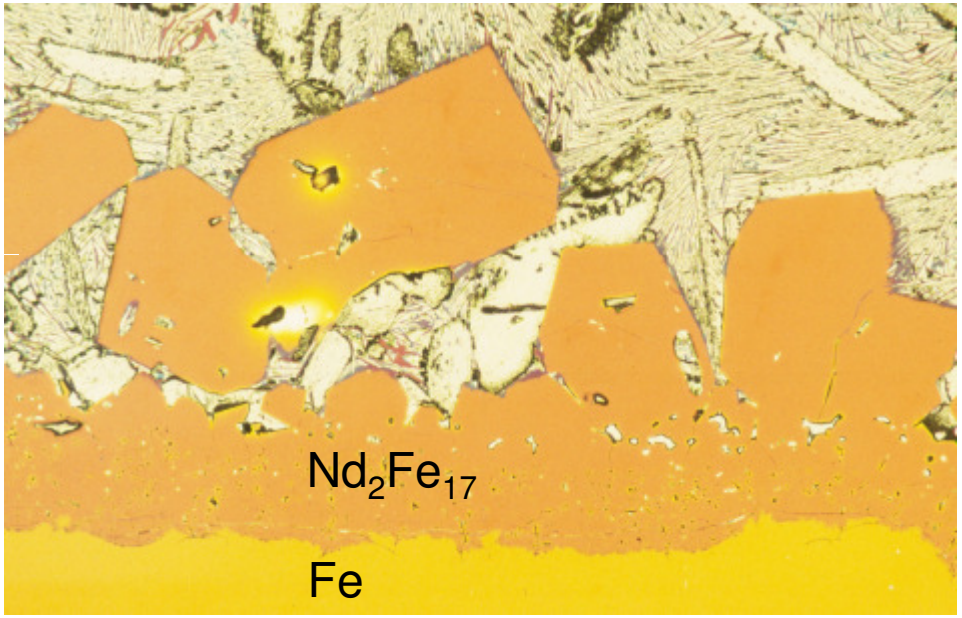
Kerr microscope image
$Nd_2Fe_{14}B$, 1000x, oil pole



Kerr microscope image
$Nd_2Fe_{14}B$, 100x

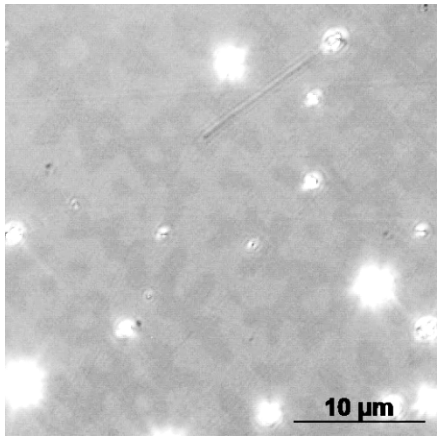
Diffusion Couple – Binary System Fe-Nd



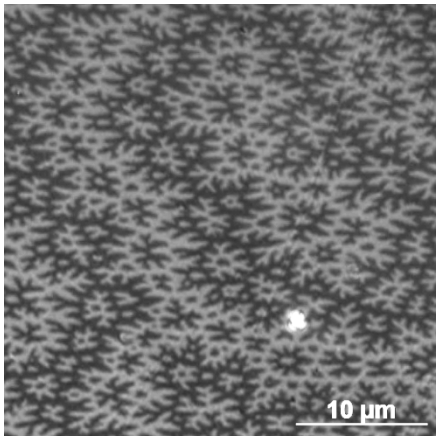


According to the phase diagram all phases are found.

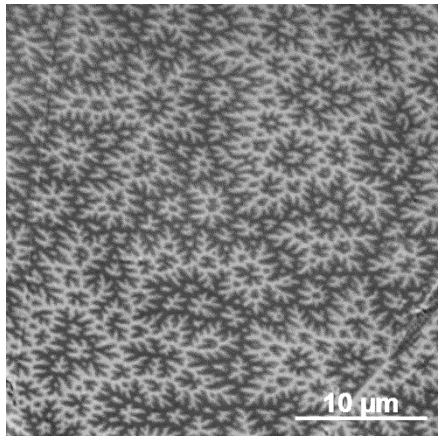
Saturation polarization J_S from domain contrast



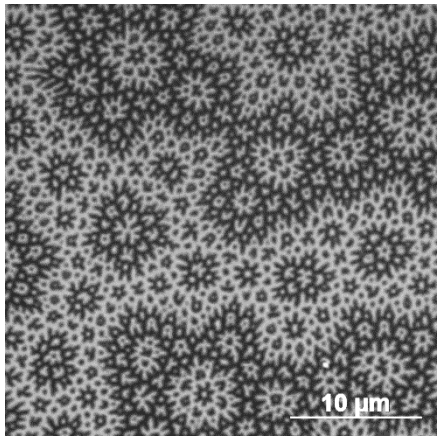
$BaFe_{12}O_{19}$ (hard ferrite)



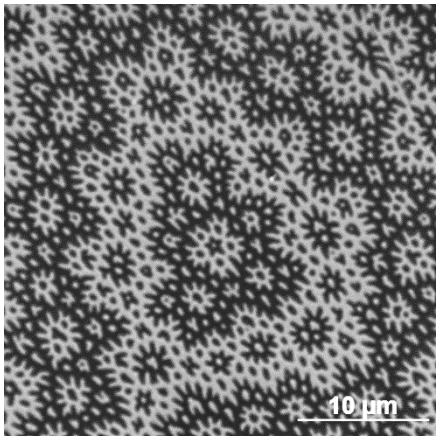
$Ce_2Fe_{14}B$



$Y_2Fe_{14}B$



$Pr_2Fe_{14}B$



$Nd_2Fe_{14}B$

Literature values	J_S (T)
$BaFe_{12}O_{19}$	~0,3
$Ce_2Fe_{14}B$	1,17
$Y_2Fe_{14}B$	1,38
$Pr_2Fe_{14}B$	1,56
$Nd_2Fe_{14}B$	1,61